

Kinetics of gas phase synthesis of ethyl-*tert*-butyl ether (ETBE) on Wells–Dawson catalyst

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Received 25 April 2006; received in revised form 29 June 2006; accepted 6 July 2006

Available online 22 August 2006

Abstract

Mechanism and kinetics of gas phase synthesis of ethyl-*tert*-butyl ether (ETBE) over Wells–Dawson heteropolyacid $H_6P_2W_{18}O_{62}$ in an anhydrous system have been discussed. The rates of ETBE synthesis were measured in a differential reactor for ethanol–isobutene system, far from the limitation by chemical equilibrium. In the pressure range studied, kinetic measurements show that isobutene has an enhancing effect on the reaction while ethanol has an inhibitory one.

Catalytic and sorption experiments allowed to formulate the mechanism of ETBE synthesis which assumed isobutene adsorption and oligomerization at the surface of heteropolyacid crystallites and the formation of carbocation using protons supplied from the bulk of catalyst. Kinetic equations were deduced indicating that it is the concentration of protons forming inter-anionic bonds between heteropolyacid anions which determines the catalytic activity of heteropolyacid.

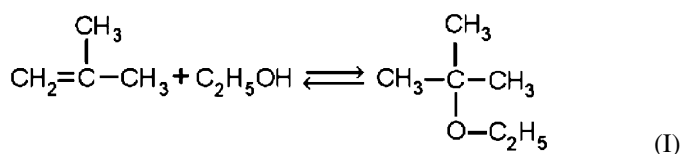
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Keywords: ETBE; Wells–Dawson; Heteropolyacid; Ethanol; Isobutene

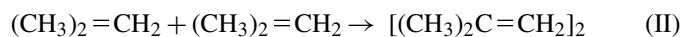
1. Introduction

Protection against the pollution of the atmosphere and soils has necessitated progressive changes in petrol composition in recent years. Lead additives which have traditionally been used to increase octane number are replaced by oxygenated compounds; especially tertiary ethers used as the antiknocking additives to automotive fuel. Introduction of oxygen to the gasoline pool via these ethers is thus feasible. Ethers with high molecular mass have lower vapor pressure and high boiling point, which is advantageous for gasoline blending. Methyl-*tert*-butyl ether (MTBE), made in the liquid phase reaction of methanol and isobutylene over an acid catalyst, is the most popular fuel additive. However, in recent years, for environmental reasons, objections have been raised against its use. Ethyl-*tert*-butyl ether (ETBE) is considered to degrade faster than MTBE in soils and water. The advantage of the ETBE use is also that one of its substrates, ethanol, may come from renewable sources, from fermentation processes. Hence the interest in the wider appli-

cation of ETBE is growing. ETBE was first synthesized from ethanol and *tert*-butanol in 1932 [1] and from isobutene (C4) and ethanol (EtOH) in 1936 [2]. The basic reaction combines ethanol and isobutene to form ETBE (reaction I).



ETBE reaction system can also include side reactions: the dimerization of isobutene to produce diisobutene as a by-product (reaction II) and formation of *tert*-butyl alcohol (TBA, reaction III). However, the formation of diisobutene is essentially eliminated when ethanol is in excess over isobutene:



Liquid phase synthesis of ETBE has been the subject of extensive research in recent years, when its thermodynamics [3] as well as kinetics [3–6] were studied. The gas phase synthesis of ETBE over acid catalysts such as zeolites [7,8] and macroporous

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sulfonic resins: Amberlyst-15, Amberlyst-35 [9], Lewatit SPC 118 and Duolite C26 [10] were also investigated, including the thermodynamic and kinetic aspects. Larsen studied the synthesis on H-mordenite [7] using absolute ethanol as the reactant. IR studies were used by him to analyze the state of the catalyst under reaction conditions and coupled with the reaction kinetics study. As the catalyst for ETBE formation H-ZSM-5 was also used [8]. Alcántara proposed the detailed mechanism of reaction basing on the description of ethanol and isobutene behavior in H-ZSM-5 channels.

Another group of acid catalysts are heteropolyacids (HPA). They catalyze a large number of acid–base and oxidation organic reactions, both in solution and gas phase. Heteropolyacids were studied in MTBE gas phase synthesis [11–13] and appeared to be selective and active catalysts at 40 °C. However, much less attention has been focused on the gas phase synthesis of ETBE on heteropolyacids. Only two papers [14,15] in literature concerning the ETBE synthesis in vapor-phase on the heteropolyacid $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ especially on the composite film catalysts such as [$\text{H}_3\text{PMo}_{12}\text{O}_{40}$ -polymer] (where the polymers: polyphenylene oxide and polysulfone were used as support) were published. The catalytic activity and stability of phosphomolibdic heteropolyacid were improved by mixing it with polymer and obtaining the membrane heteropolyacid–polymer composite film.

In the recent years increasing attention has been paid to Wells–Dawson type octadeca heteropolyacid catalysts, mainly $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, which are considered to exhibit better catalytic properties than those of Keggin type dodeca heteropolyacids. The latter have been until now the predominant object of studies in the field of catalysis on polyoxometallates.

$\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ appeared to be an effective catalyst in MTBE liquid [16] and gas [17] phase synthesis. The only publications concerning ETBE synthesis on Wells–Dawson heteropolyacid were Refs. [18,19] published with the participation of the present author. Both deal with gas phase reaction for which crystalline [18] and supported [19] $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ catalysts were used. In both only the activity was determined based on dependence to catalyst's pretreatment temperature (the former one) and the textural properties of the supports (the last one) but no kinetic aspects were studied.

The aim of the present publication was to relate a study of the kinetics of gas phase formation of ETBE by ethanol to isobutene addition at the absence of water, both in the feed, and in the solid catalyst as the water of crystallization. The effect of water in the catalytic system which was signaled by us in Ref. [18] deserves separate attention because water which formally does not participate in the catalytic reaction may shape the secondary structure of HPA and also influence the equilibrium in the bulk between protons and absorbed ethanol molecules. The knowledge of reaction occurring at the absence of water seems essential for the study of the effect of water which will be the object of the following paper. In the present publication the experiments were carried out using heteropolyacid samples of stoichiometric composition $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ devoid of water of crystallization and preheated at temperature low enough to avoid its dehydroxylation (departure of so called water of constitution).

2. Experimental

Ethyl alcohol absolute pure (99.8 wt.%, the content of 0.07 wt.% H_2O was determined by chromatographic analysis) supplied by POCh Gliwice, 2-methyl propene (isobutene, *i*- C_4H_8 , p.a., Aldrich) and ETBE (99%, Aldrich) were used in the sorption and catalytic experiments.

The sample of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot n\text{H}_2\text{O}$ was synthesized according to Refs. [17,20] and was kept at room temperature in a desiccator over a saturated solution of $\text{Mg}(\text{NO}_3)_2$. DTG analysis of the sample was done using a TGA/SDTA 851° Mettler–Toledo apparatus. Heating rate was 5 °C min^{-1} . Thermal analysis showed that the composition of the equilibrated sample corresponded to $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 31\text{H}_2\text{O}$. The sample was dehydrated by heating at 220 °C 2 h [18].

Specific surface area of anhydrous Wells–Dawson acid, after preheating at 220 °C 2 h, was determined using Quantachrome Autosorb Gas Sorption System by nitrogen sorption at 77 K.

Sorption of ethyl alcohol and isobutene was studied by means of a quartz spring sorption balance (sensitivity 0.6828 mm mg^{-1}) connected with a vacuum system. The elongation of the spring was measured with a cathetometer, the sensitivity of which was 0.01 mm.

A quartz constant flow differential microreactor ($\phi = 10$ mm) was used for catalytic experiments. The helium carrier gas was first saturated with ethanol vapour and subsequently mixed with a stream of isobutene. The composition of the reaction mixture (isobutene/ethanol molar ratio) was in the range 0.35–1.21. The catalytic reactor was connected on line with Perkin–Elmer AutoSystem XL gas chromatograph and a Porapak QS column was used for the chromatographic analyses. Samples of 0.057 g (0.034 cm^3) of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot 31\text{H}_2\text{O}$ (13×10^{-6} mol) were mixed with 0.36 g (0.37 cm^3) of quartz grains ($\phi = 0.19$ mm) thus obtaining a catalyst layer of 0.5 cm thick. Before the catalytic experiments the samples were preheated in situ in a catalytic reactor (e.g. in helium flow 30 ml min^{-1}).

Catalytic experiments were carried out in the steady state, far from the limitation by chemical equilibrium, at 35–80 °C. Temperature was kept by temperature programmer MRT-4 (accuracy ± 0.1 °C) and was controlled by the thermo-couple located in the reactor jacket close to the catalyst bed. The conversions (<10%) were measured free from the influence of external mass transfer and diffusion. The partial pressures of reactants were: for isobutene 9–20 kPa and for ethanol 15–26 kPa and W/F (where W is the catalyst weight and F the total flow rate) was between 0.024 and 0.036 g h mol^{-1} .

3. Results

Fig. 1 shows a typical catalytic run and Fig. 2 the dependence of isobutene conversion on the catalyst's mass. It is seen that the latter was linear for the samples up to 0.15 g on which conversion of isobutene was about 30%. Hence in order to assure the elimination of the external diffusion effects in all kinetic measurements the samples of 0.05 g were used.

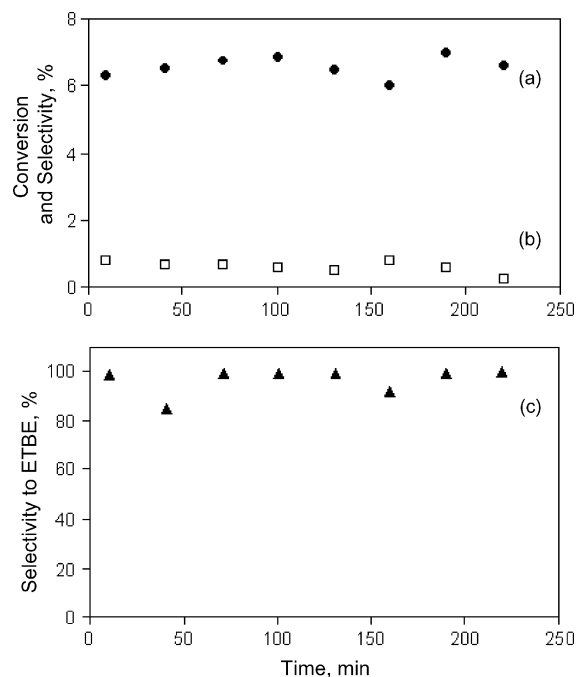


Fig. 1. (a) Isobutene conversion, (b) selectivity to TBA and (c) selectivity to ETBE vs. time of catalytic test ($p_{C_4} = 10$ kPa, $p_{EtOH} = 26$ kPa) at 40 °C.

The plot in Fig. 3 shows the isobutene conversion against reaction temperature. The catalyst was already active at temperature as low as 35 °C, its activity passed over a maximum between 40 and 50 °C. Such behavior is typical of the reversible exothermic reactions and the descending branch of the plot corresponds to the situation when the observed isobutene conversion approaches the equilibrium conversion calculated using thermodynamic data given in Ref. [21] (represented by the dotted line in Fig. 3) and the effect of reverse reaction, ETBE decomposition, can not be neglected. On the other hand at 35 or 40 °C equilibrium conversion reached 48.7% or 41.9%, respectively, and the use of 0.05 g of samples the conversion never exceeded 10% the effect of reverse reaction could be practically neglected. This is why the temperature of 40 °C has been chosen as the temperature of catalytic kinetic measurements.

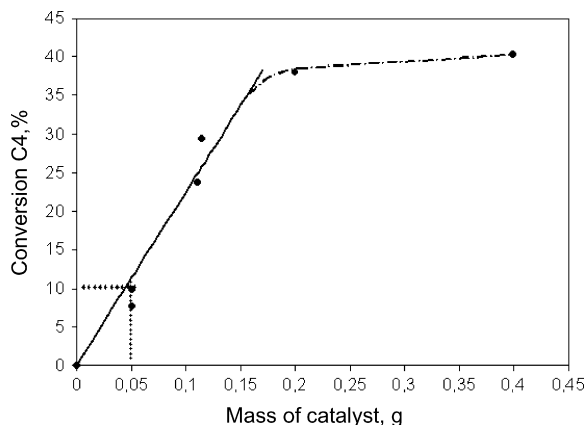


Fig. 2. External diffusion effects of Wells–Dawson sample.

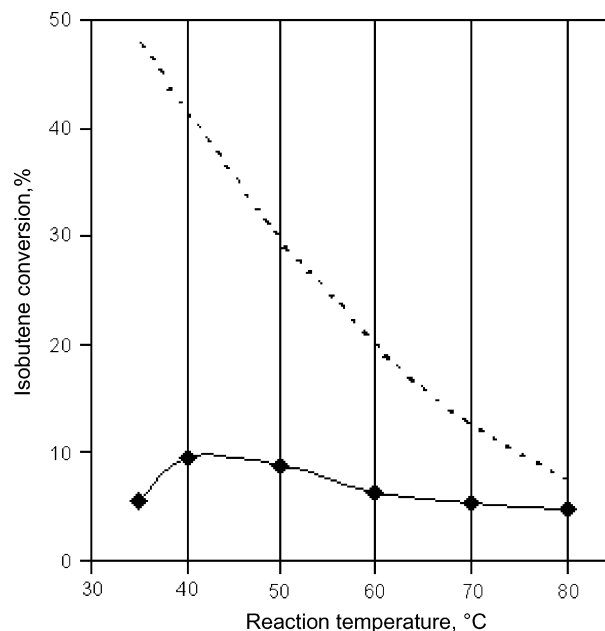


Fig. 3. Dependence of yield of ETBE as a function of the reaction temperature at $p_{EtOH} = 17.7$ kPa and $p_{C_4} = 14.6$ kPa. Dotted line presents the equilibrium yield of ETBE calculated using the equilibrium constants determined by Iborra et al. [22].

Fig. 4 presents the course of ethanol vapour sorption by $H_6P_2W_{18}O_{62}$ at 40 °C. Prior to the experiments the 0.05 g sample was dehydrated in situ by evacuation for 2 h at 220 °C. Such pretreatment resulted in complete removal of the water of crystallization without dehydroxylation of acid. Sorption of ethanol vapour was measured within the pressure range 1.5–6.3 kPa which was stepwise increased after equilibrium had been reached. The desorption run was started by pumping off the system without changing the temperature. In Table 1 the obtained in ethanol sorption experiments carried out at 22 and 40 °C are given. The amount of uptaken ethanol is expressed as the number of ethanol molecules per one proton in the sample, but in the brackets also the corresponding number of ethanol monolayers is given. The latter was calculated using the BET surface area of dehydrated sample equal to 3.6 m² g⁻¹ and assuming the surface covered by one C₂H₅OH molecule as

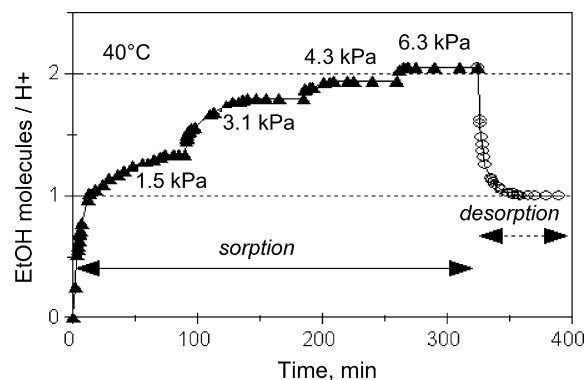


Fig. 4. Sorption and desorption stages of ethanol at different pressures on anhydrous $H_6P_2W_{18}O_{62}$ at 40 °C.

Table 1
Sorption of ethanol on Wells–Dawson acid at 22 and 40 °C and different pressures and the equations of Freundlich isotherm

Sorption or desorption temperature (°C)	Ethanol vapour pressure (kPa)	Number of EtOH molecule/H ⁺ (number of layers)		Freundlich isotherm c (EtOH/H ⁺)
		Absorbed	Remaining after desorption	
22	1.5	1.15 (9.0)		$c = 0.9p_{\text{EtOH}}^{0.51 \pm 0.04}$
	2.8	1.58 (12.6)		
	4.4	1.89 (15.1)		
	5.9	2.39 (19.2)	1.00 (7.7)	
40	1.5	1.33 (14)		$c = 1.2p_{\text{EtOH}}^{0.31 \pm 0.05}$
	3.1	1.79 (18.5)		
	4.3	1.94 (19.9)		
	6.3	2.05 (21)	0.99 (10.8)	

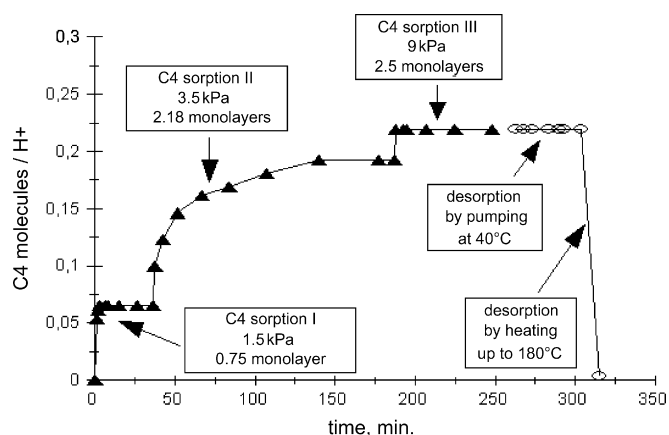


Fig. 5. Sorption of isobutene on $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ at different pressures at 40 °C and desorption by pumping at 40 °C and by heating up to 180 °C.

$2.1 \times 10^{-19} \text{ m}^2$. In both cases of temperature the results could be well fitted in an empirical Freundlich type isotherm.

Fig. 5 shows sorption of isobutene on anhydrous $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ at 40 °C. After reaching equilibrium at $p_{\text{C}_4} = 1.5 \text{ kPa}$ the pressure has been increased to 3.5 kPa and similarly to 9 kPa. After two hours at these latter conditions the sample was evacuated. No desorption was observed at 40 °C and it was necessary to raise temperature to 150–180 °C in order to achieve complete desorption.

Fig. 6 shows the course of an experiment in which the effect of presorption of ethanol on the sorption of isobutene was examined. In Fig. 6A sorption of isobutene at 40 °C and $p_{\text{C}_4} = 9 \text{ kPa}$ on anhydrous $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ without preadsorbed ethanol was studied. Isobutene uptake corresponded to 0.22 C_4H_8 molecules per one proton which was equivalent to the sample coverage with 2.6 monolayers which was much lower than that corresponding to ethanol. Fig. 6B shows the course of ethanol preadsorption at $p_{\text{EtOH}} = 1.3 \text{ kPa}$ also at 40 °C. After reaching saturation the sample was evacuated. Ethanol partly desorbed. The amount of irreversibly bonded $\text{C}_2\text{H}_5\text{OH}$ corresponded to 0.8 ethanol molecules per one proton. In the next step isobutene was introduced at $p_{\text{C}_4} = 9 \text{ kPa}$ and its sorption registered. It is seen that presorption of ethanol did not change isobutene sorption capacity of the heteropolyacid.

In order to check the reactivity of the adsorbed isobutene the experiment illustrated by Fig. 7 has been carried out. The sample of HPA was saturated at first with ethanol at 4.7 kPa, evacuated and then contacted with isobutene at 11.7 kPa at 40 °C then evacuated and a portion of ethanol vapour at $p_{\text{EtOH}} = 3.1 \text{ kPa}$ was introduced. A decrease of the weight has been observed at first which was interpreted as the removal of C_4H_8 by the formation of ETBE given off to the gas phase. After 14 min a slow increase of weight was registered this was ascribed to the sorption of ethanol by the sample.

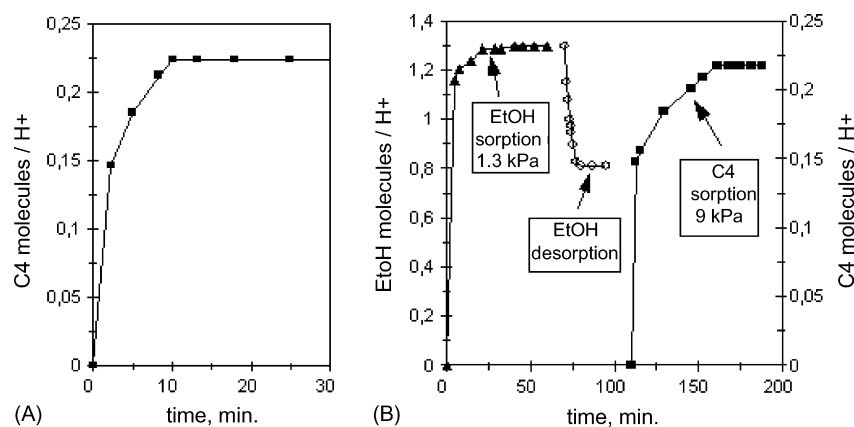


Fig. 6. Sorption of reactants by Dawson sample at 40 °C: (A) isobutene (■) at 9 kPa, (B) isobutene at 9 kPa (■) after pre-adsorption of irreversibly bonded ethanol (▲: sorption; ○: desorption).

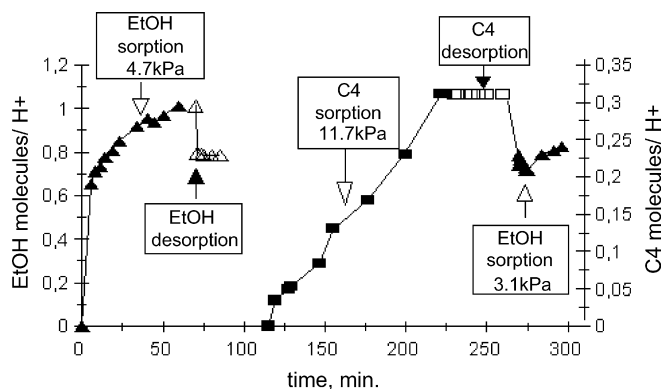


Fig. 7. Sorption-desorption curves of reactants on $H_6P_2W_{18}O_{62}$: (\blacktriangle) ethanol sorption at 4.7 kPa (0–70 min) and at 3.1 kPa (260–300 min), (\triangle) ethanol desorption, (\blacksquare) isobutene sorption at 11.7 kPa, (\square) isobutene desorption.

4. Discussion

As Fig. 1a and b shows solid $H_6P_2W_{18}O_{62}$ devoid of the water of crystallization is an active and selective catalyst for gas phase synthesis of ETBE and does not suffer deactivation over the period of several hours. The only by-product detected (Fig. 1b) were the traces of *tert*-butyl alcohol (TBA).

The rate of ETBE formation was expressed as:

$$r = F \frac{x}{m}$$

where F is the velocity of isobutene flow in the feed (mol h^{-1}), x the ratio of isobutene conversion, and m is the mass of anhydrous Dawson acid (g). Its dependence on the partial pressures of ethanol, and isobutene is presented in Figs. 8 and 9 in double logarithmic scales. The slopes of the linear plots are experimental orders of reaction with respect to isobutene and ethanol. Considering their values given in Table 2 empirical rate equation can be given:

$$r = k p_{\text{EtOH}}^{1.64} p_{\text{C}_4}^{-2.00} \quad (\text{IV})$$

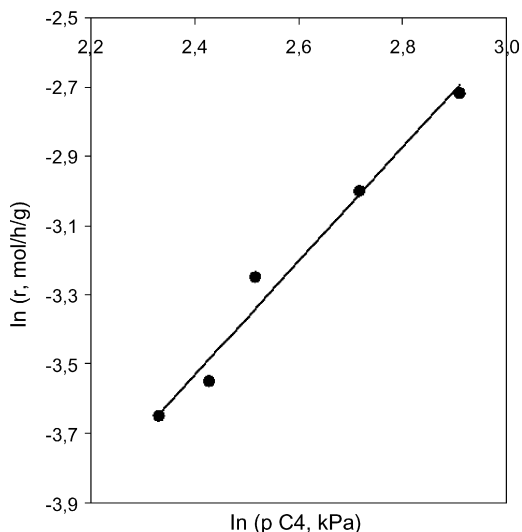


Fig. 8. Logarithmic plot of rate of isobutene conversion at 40 °C vs. isobutene partial pressure at constant ethanol pressure ($p_{\text{EtOH}} = 17.2 \text{ kPa}$).

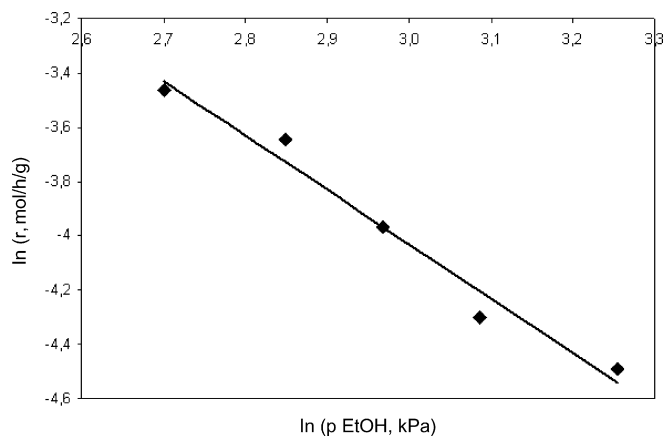


Fig. 9. Logarithmic plot of rate of isobutene conversion at 40 °C vs. ethanol partial pressure at constant isobutene pressure ($p_{\text{C}_4} = 9.9 \text{ kPa}$).

It is seen that the reaction order with respect to isobutene is positive and reaction rate does increase with the increase of isobutene partial pressure (Fig. 8) while the reaction order with respect to ethanol partial pressure is negative and reaction rate decreases with the increase of ethanol partial pressure (Fig. 9). The latter is a rather rare case in chemical kinetics.

Similar unique behavior of ethanol in the case of heteropolyacids has been observed by Lee [22] who stated that the rate of ethanol dehydration on $H_3PW_{12}O_{40}$ was increasing with the C_2H_5OH partial pressure up to a certain value but decreased in the region of high ethanol partial pressure. This was explained by the assumption that it is only the protonated ethanol monomers and dimers, forming in the pseudoliquid phase at lower ethanol pressures, which are active in the catalytic process. On the other hand at high ethanol pressures non-active larger clusters predominate and the concentration of monomers and dimers decreases.

The positive effect of methanol partial pressure in its lower range and negative in higher partial pressure range on the methyl-*tert*-butyl ether formation on several heteropolyacids ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_5BW_{12}O_{40}$, $H_6P_2W_{18}O_{62}$) was observed by Shikata et al. [11]. They assumed that sorption of methanol by the bulk of heteropolyacid crystallites at the contact with methanol-isobutene feed expanded their crystal lattice and enabled its penetration by isobutene molecules. Hence, reaction could be assumed to occur in bulk, in the so called pseudoliquid state. Within low methanol pressure range its increase would accelerate reaction by increasing the concentration of catalytically active protonated monomers and dimers. On the other hand increasing methanol partial pressure over a certain limit would gradually increase the concentration of non-active larger protonated clusters $(CH_3OH)_nH^+$ with $n \geq 3$ and decelerate methanol to isobutene addition.

Table 2
Experimental reaction orders

Reaction order	Value	Correlation coefficient
With respect to ethanol	-2.00 ± 0.19	0.974
With respect to isobutene	1.64 ± 0.14	0.979

The gas phase formation of MTBE on solid $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was studied in Ref. [11]. In this research a positive reaction order with respect to methanol was observed at the initial stage of the catalytic reaction when the concentration of methanol in the bulk of HPA crystallites was either 0 or very low. On the other hand this reaction order became negative when steady states of reaction at different methanol partial pressures and different methanol bulk concentrations were taken for the calculations. The independent sorption experiments did not confirm the penetration of isobutene into the bulk of HPA crystallites with pre-sorbed methanol. Hence it was assumed that reaction occurs between isobutene adsorbed at the surface and methanol supplied from the bulk. In organic chemistry reaction of methanol with isobutene is classified as electrophilic addition in which one of the steps includes the formation of carbocation. Hence it was assumed that isobutene at the surface is protonated with protons supplied from HPA. Basing on IR and sorption measurements [23] it could be assumed that protons in the bulk are partly bonded in protonated methanol clusters and partly forming relatively weak hydrogen bonds between HPA anions. For such a catalytic system model a kinetic equation has been derived which shows the dependence of reaction orders on the average number of CH_3OH molecules in the protonated cluster and hence on the concentration of CH_3OH in the bulk of solid governed by the methanol partial pressure in the feed.

The discussion of the mechanism of ETBE synthesis on Dawson heteropolyacid has to be preceded by an overview of the behavior of reagents, ethanol and isobutene at the contact with the catalyst.

Sorption of ethanol on dehydrated $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ at 40°C is presented in Fig. 4. It is rapid up to the uptake of about one $\text{C}_2\text{H}_5\text{OH}$ molecule per one proton in the sample. The subsequent portions of ethanol vapour introduced are absorbed more slowly and the equilibrium reached with increasing p_{EtOH} approached the value of two ethanol molecules per one proton. The amount of uptaken ethanol expressed as the corresponding number of monolayers as high as 20 indicates rather the predominant bulk than surface sorption. At 40°C sorption of ethanol is partly reversible; the sorption irreversible at these conditions corresponds to one ethanol molecule per one proton. This is the behavior typical of bulk sorption of alcohols on heteropolyacids and the formation of protonated ethanol clusters: monomer $\text{C}_2\text{H}_5\text{OH}_2^+$ and dimer $[(\text{C}_2\text{H}_5\text{OH})_2\text{H}^+]$. The protonation of ethanol on its sorption on dehydrated $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ has been confirmed by infrared spectroscopy detecting the ethoxonium ion signaled by 1520 cm^{-1} band [24,25]. Parallel to the formation of 1520 cm^{-1} band the bands at 2400 and 2140 cm^{-1} ascribed to the hydrogen bonds between HPA anions vanished and a new band at 3400 cm^{-1} appeared ascribed to hydrogen bonds between HPA anions and protonated clusters, thus confirming proton transfer from inter-anionic hydrogen bond to the ethanol clusters. Volume sorption and protonation of ethanol does create new secondary structure of heteropolyacid in analogy to the formation of the heteropolyacid hydrates.

The course of isobutene sorption at 40°C is presented in Fig. 5. It is seen that at the lowest isobutene pressure sorption was rapid and equilibrium reached after only 2 min. The fol-

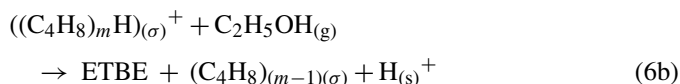
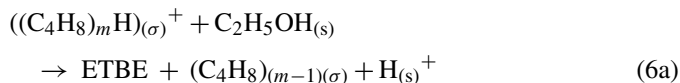
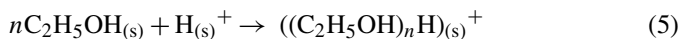
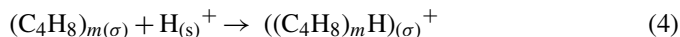
lowing portion of adsorbate was consumed more slowly and the equilibrium reached at $p_{\text{C}_4} = 3.5\text{ kPa}$ was not very distant from that reached at $p_{\text{C}_4} = 9\text{ kPa}$. Sorption at this stage was irreversible at 40°C and it was necessary to heat up to $150\text{--}180^\circ\text{C}$ in order to remove all isobutene from the sample. Generally sorption of isobutene was much lower than that of ethanol. The amount of isobutene uptaken at 9 kPa corresponded to the formation of 2.6 monolayers while similar estimation in the case of ethanol vapour sorption at $p_{\text{EtOH}} = 6.3\text{ kPa}$ corresponded to 21 monolayers being the indication that ethanol penetrated exclusively or partly the bulk of HPA crystallites. The amount of isobutene corresponding to 2.6 monolayers may be expected in two cases: either isobutene would penetrate the bulk or remain at the surface in a form of a multilayer. The fact that its adsorption was irreversible would indicate its oligomerization. As Fig. 6B shows sorption of isobutene was independent of presorption of ethanol changing (expanding) the secondary structure of crystalline heteropolyacid. This may be taken as an argument against the penetration of isobutene into the bulk. The two other facts: low dipole moment of isobutene ($\mu_{\text{C}_4} = 0.50\text{ D}$) and the size of its molecules, larger than that of ethanol ones ($\mu_{\text{EtOH}} = 1.69\text{ D}$), also support the expectation that isobutene remains adsorbed at the surface.

Fig. 6B also shows that the weight of a sample with irreversibly bonded ethanol does not diminish its weight on the contact with isobutene vapour but only the increase of weight is observed. These facts suggest that irreversibly bonded ethanol does not react with isobutene in the gas phase. On the other hand, the experiment shown in Fig. 7 shows that when a sample covered with isobutene (sample with irreversibly pre-absorbed ethanol) comes in contact with gaseous ethanol, the weight does decrease at first, but after some 14 min it begins to increase. This indicates that we deal with two processes: reaction of ethanol from gas phase with adsorbed isobutene and sorption of ethanol. At the first stage the first process is more rapid but then slows down and the second one becomes predominant.

All the above mentioned experimental results allow us to propose a model of catalytic system in which ETBE formation occurs on anhydrous $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ by addition of ethanol to isobutene. It is generally accepted in organic chemistry that this is an electrophilic addition i.e. occurring with the formation of a carbocation as the intermediate species. In the model for which the kinetic calculations will be presented it is assumed that polar ethanol penetrates the bulk of HPA crystallites forming the protonated clusters and isobutene weakly polar remains at the surface as monomers and/or oligomers partly protonated as C_4H_9^+ or $(\text{C}_4\text{H}_8)_m\text{H}^+$. Protons forming such protonated ethanol clusters and carbocations at the surface are supplied by the solid in which, they are forming weak hydrogen bonds between HPA anions (weakly bonded protons). It is also assumed that catalytic reaction occurs between carbocations at the surface and neutral ethanol molecules supplied either directly from gas phase or from the bulk.

In such system the following reaction steps should be taken into account:





(where g and s are the molecules in the gas or solid phase, σ the molecule adsorbed at the surface, m the number of isobutene molecules in oligomer, n is the number of ethanol molecules in protonated cluster; $m, n = 1, 2, 3, \dots$).

Each of the enumerated steps may comprise several elementary reactions. For example Eq. (5) consists in fact of a series of equations for different integral values of n .

Let us now assume—as it is usually done in organic chemistry that the formation of carbocation is the slowest step [26] and hence reaction (4) is the rate determining step. Reaction rate would be then:

$$r = k_4 [(\text{C}_4\text{H}_8)_m_{(\sigma)}] [\text{H}_{(\text{s})}^+] \quad (7)$$

At stationary state virtual equilibriums of reactions (1) and (3) are assumed:

$$K_1 = \frac{[\text{C}_4\text{H}_8_{(\sigma)}]}{p_{\text{C}_4}} \quad \text{and} \quad K_3 = \frac{[(\text{C}_4\text{H}_8)_m_{(\sigma)}]}{[\text{C}_4\text{H}_8_{(\sigma)}]^m} \quad (8)$$

The values of $[\text{C}_4\text{H}_8_{(\sigma)}]$ and $[(\text{C}_4\text{H}_8)_m_{(\sigma)}]$ calculated from the above equations are substituted in the Eq. (7) which transforms into:

$$r = k_4 K_1^m K_3^m p_{\text{C}_4}^m [\text{H}_{(\text{s})}^+] \quad (9)$$

where $[\text{H}_{(\text{s})}^+]$ is the concentration of the protons forming hydrogen bonds between Wells–Dawson anions and assumed to be more weakly bonded than protons in protonated ethanol clusters. It should be mentioned here that in Ref. [23] it has been shown on the basis of thermometric titration that the enthalpy of methanol protonation to CH_3OH_2^+ in the bulk of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ crystallites was 58.9 kJ mol^{-1} and that of addition of the second methanol molecule ($\text{CH}_3\text{OH}_{2(\text{s})}^+ + \text{CH}_3\text{OH}_{(\text{g})} \rightarrow ((\text{CH}_3\text{OH})_2\text{H}^+)_{(\text{s})}$) 53.5 kJ mol^{-1} . No such measurements were carried out with ethanol sorption in $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ but it is considered that similar qualitative relations exist also in this latter case. The transfer of protons from hydrogen bonds in $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ to the ethanol molecules was confirmed by the infrared investigation in Ref. [25]. In this paper formation of $\text{C}_2\text{H}_5\text{OH}_2^+$ (IR band 1520 cm^{-1}) was accompanied by the vanishing of the 2400 and 2140 cm^{-1} bands, which are characteristic for hydrogen bonds in the dehydrated $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$. Simultaneously a band at 3400 cm^{-1} appeared signaling a new array of hydrogen bonds.

In the model proposed in the present paper the loosely bonded protons $\text{H}_{(\text{s})}^+$ are playing in fact the role of catalytically active centers. The concentration of protons is determined by the equilibrium between protons bonded in the inter-anionic bonds $\text{O}-\text{H}^+-\text{O}$, protons bonded in the protonated clusters of ethanol $(\text{C}_2\text{H}_5\text{OH})_n\text{H}_{(\text{s})}^+$ and, in much lower number, protons bonded in the carbocation $(\text{C}_4\text{H}_8)_m\text{H}^+$. The concentration of $[\text{H}_{(\text{s})}^+]$ was expressed using the equation:

$$K_5 = \frac{[(\text{C}_2\text{H}_5\text{OH})_n\text{H}_{(\text{s})}^+]}{[\text{C}_2\text{H}_5\text{OH}_{(\text{s})}]^n [\text{H}_{(\text{s})}^+]}$$

in which concentration of ethanol molecules in the bulk of HPA was calculated from equation:

$$K_2 = \frac{[\text{C}_2\text{H}_5\text{OH}_{(\text{s})}]}{p_{\text{EtOH}}}$$

and was obtained:

$$[\text{H}_{(\text{s})}^+] = \frac{[(\text{C}_2\text{H}_5\text{OH})_n\text{H}_{(\text{s})}^+]}{[K_2 p_{\text{EtOH}}]^n K_5} \quad (10)$$

After substitution Eq. (10) into Eq. (9) the reaction rate equation would have the following form:

$$r = k_4 K_1^m K_2^{-n} K_3 K_5^{-1} p_{\text{C}_4}^m p_{\text{EtOH}}^{-n} [(\text{C}_2\text{H}_5\text{OH})_n\text{H}_{(\text{s})}^+] \quad (11)$$

If we assume that n is the number of ethanol molecules in the predominating cluster the value of $(\text{C}_2\text{H}_5\text{OH})_n\text{H}_{(\text{s})}^+$ can be approximated by the total $\text{C}_2\text{H}_5\text{OH}$ concentration in the bulk expressed by Freundlich isotherm $[(\text{C}_2\text{H}_5\text{OH})_n\text{H}_{(\text{s})}^+] \approx c = 1.2 p_{\text{EtOH}}^{0.3}$, Table 1). Fractional value of n indicates the presence of two clusters differing by one $\text{C}_2\text{H}_5\text{OH}$ molecules and contained in comparable amounts.

When isotherm equation is inserted into Eq. (11) the final equation is obtained:

$$r = \xi p_{\text{C}_4}^m p_{\text{EtOH}}^{0.3-n} \quad (12)$$

where $x = 1.2 k_4 K_1^m K_2^{-n} K_3 K_5^{-1}$.

The experimental reaction order with respect to ethanol at 40°C was equal -2.0 hence the substitution of this order into the exponent of Eq. (12) gives the value $n = 2.3$. It means that assuming that the formation of carbocation is the slowest step, mainly ethanol dimer is formed in the bulk or at least in the next-to-surface layer of HPA crystallites. As long as n is higher than 0.3 the reaction order with respect to ethanol has to be negative. When the value n is lower than 0.3 this reaction order will be positive. The calculation based on the ethanol isotherm indicates that such a situation will take place when ethanol pressure in the catalytic reactor would be lower than about 1.3 kPa . The ethanol pressure during catalytic experiments is higher than 10 kPa therefore the kinetic experiments in the reaction steady state indicate negative reaction order with respect to ethanol.

According to Eq. (12) reaction order with respect to isobutene corresponds to the value m which is simultaneously the level of isobutene oligomerization and the experimental reaction order. It should be noticed that the experimental reaction order with respect to isobutene is higher than one (equals 1.64 , Table 2) thus suggesting partial oligomerization of isobutene.

The other possible mechanism of ETBE synthesis is the mechanism in which the reaction between carbocation and neutral ethanol molecules is taken as the rate determining step. This may involve either ethanol supplied from the bulk $C_2H_5OH_{(s)}$ according to reaction (6a) or from gas phase $C_2H_5OH_{(g)}$ according to the reaction (6b).

Let now discuss the case in which reaction (6a) is taken as the rate determining step:

$$r = k_{(6a)} [((C_4H_8)_m H^+)_{(\sigma)}] [C_2H_5OH_{(s)}] \quad (13)$$

Assuming the virtual equilibrium of reactions (1), (2) and (4) the following equations were obtained:

$$K_1 : \text{Eq. (8)}, \quad K_2 = \frac{[C_2H_5OH_{(s)}]}{p_{EtOH}},$$

$$K_4 = \frac{[((C_4H_8)_m H^+)_{(\sigma)}]}{[H_{(s)}^+][C_4H_8]_{m(\sigma)}} \quad (14)$$

The concentrations of $[((C_4H_8)_m H^+)_{(\sigma)}]$ and $[C_2H_5OH_{(s)}]$ obtained, respectively, from Eq. (14) are inserted into the reaction rate Eq. (13) to obtain:

$$r = k_{(6a)} K_2 K_4 p_{EtOH} [(C_4H_8)_{m(\sigma)}] [H_{(s)}^+] \quad (15)$$

The concentration of $[H_{(s)}^+]$ was calculated from Eq. (10):

$$r = k_{(6a)} K_1^m K_2^{1-n} K_3 K_4 K_5^{-1} p_{C_4}^m p_{EtOH}^{1-n} [(C_2H_5OH)_n H_{(s)}^+] \quad (16)$$

When Freundlich isotherm equation is inserted into the Eq. (16) I obtain:

$$r = 1.2 k_{(6a)} K_1^m K_2^{1-n} K_3 K_4 K_5^{-1} p_{C_4}^m p_{EtOH}^{1-n+0.3} \quad (17)$$

and by inserting $\beta = 1.2 k_{(6a)} K_1^m K_2^{1-n} K_3 K_4 K_5^{-1}$ to Eq. (17) the final reaction rate equation appears as the formula:

$$r = \beta p_{C_4}^m p_{EtOH}^{1.3-n} \quad (18)$$

Eq. (18) has a similar form to Eq. (12) however in this case the value $n = 3.3$ is higher and the values of constants are different. It suggesting that trimer species $(C_2H_5OH)_3 H^+$ are the predominant clusters of ethanol in the bulk of Dawson-type heteropolyacid.

The assumption that the reaction (6b), between carbocation and ethanol supplied from gas phase (Rideal's mechanism) is the rate determining step allowed obtaining the rate equation:

$$r = \gamma p_{C_4}^m p_{EtOH}^{1.3-n} \quad (19)$$

where rate constant $\gamma = 1.2 k_{(6b)} K_1^m K_2^{-n} K_3 K_4 K_5^{-1}$ is different than rate constant $\beta = 1.2 k_{(6a)} K_1^m K_2^{1-n} K_3 K_4 K_5^{-1}$ in Eq. (18) but the reaction orders with respect to ethanol have the same value $(1.3 - n)$.

The derived kinetic equations (Table 3) have the same mathematical form which is in agreement with the empirical formula (Eq. (IV)). This fact indicates the authenticity of the assumed models. According to the above considerations, protons exist in the form of protonated clusters of ethanol, the carbocation

Table 3
Formulated kinetic equations

Mechanism of rate determining step	Equations
Carbocation formation reaction (4)	$r = x p_{C_4}^m p_{EtOH}^{0.3-n}$
Surface reaction of ETBE formation, ethanol supplied from the bulk reaction (6a)	$r = \beta p_{C_4}^m p_{EtOH}^{1.3-n}$
Surface reaction of ETBE formation, ethanol supplied from gas phase reaction (6b)	$r = \gamma p_{C_4}^m p_{EtOH}^{1.3-n}$

species as well as protons linking heteropolyacid anions. The reaction rate distinctly depends on the concentration of the latter (Eqs. (9) and (15)) which on the other hand is regulated by the concentration of ethanol in the bulk of HPA (Eq. (13)). It means that the proton transfer plays an essential role in ETBE synthesis. Protons forming inter-anionic bond in HPA are in fact the catalytically active centers.

5. Conclusions

Reaction rate of ETBE synthesis depends firstly on the concentration of reagents in the feed, secondly on catalyst's sorption properties. Particularly it depends on the ability of ethanol absorption into the crystal lattice of Wells–Dawson heteropolyacid and forming the protonated ethanol clusters. The absorption of ethanol reduces the activity of catalyst because the formation of ethanol clusters decreases the concentration of weakly bonded protons linking heteropolyacid anions and resulting in the negative order with respect to ethanol. Comparing the value of experimental reaction order with respect to ethanol with reaction order derived from kinetic equations, the formation of ethanol cluster in the form of dimer and trimer was calculated, and is in agreement with sorption data.

The second reactant isobutene remains at the surface of the catalyst. Reaction order with respect to isobutene is higher than one thus suggesting oligomerization of one $(C_4H_8)_m$ which on further reaction of ethanol would produce one molecule of ETBE and regenerate one molecule of isobutene oligomer $(C_4H_8)_{(m-1)}$. Mechanism assumed that reaction occurs at the surface of $H_6P_2W_{18}O_{62}$ crystallites between adsorbed isobutene in the form of carbocation oligomers and ethanol supplied from the bulk else ethanol in the gas phase. The type of protonated species $(C_2H_5OH)_n H^+$ or $(C_4H_8)_m H^+$ depends on the ethanol concentration in the gas phase. Both the surface and the bulk of the catalyst participate in ether synthesis and from this point of view the studied catalytic system was relatively complicated.

Acknowledgement

I would like to acknowledge Prof. Adam Bielański for his valuable remarks and fruitful discussion. This work was financially by the Ministry of Scientific Research and Education Grant No. N204 164 31/3689.

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