# Kinetics of the Synthesis of Propyl and Butyl Acrylates in the Presence of Some Heteropolyacids as Catalysts

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ABSTRACT: Esterification reactions of acrylic acid with *n*-propanol and *n*-butanol were carried out in the liquid phase in the presence of $H_3PW_{12}O_{40}$ or $H_3PMo_{12}O_{40}$ as a catalyst, at various temperatures, molar ratios of the reactants, and concentrations of the catalyst. The kinetic equations had a nonelementary form. © 2008 Wiley Periodicals, Inc. Int J Chem Kinet 41: 12–17, 2009

## INTRODUCTION

Acrylates are important intermediates in the production of plastics. Owing to the diverse properties of polymers and the copolymers obtained on their basis, they have a wide application in everyday life and in many industries. Esterification of acrylic acid with alcohol has commercially been performed by using liquid catalyst such as sulfuric acid, hydrofluoric acid, and para-toluenesulfonic acid, but these are toxic and corrosive. Heteropolyacids are known to be highly active acidic catalysts in solution, and so they have been successfully used in an acid reaction such as esterification. Heteropolyacids are less toxic. Replacing mineral acids with heteropolyacids offers a means for eliminating or at least reducing the dangers that those conventional catalysts of esterification cause to the natural environment.

While the technological aspects of the esterification of acrylic acid with propyl and butyl alcohols have been relatively well understood, the knowledge of the kinetics and thermodynamics of this process still remains inadequate. There are practically no data on the kinetics of the synthesis of propyl and butyl acrylate in the presence of heteropolyacids. Only Chen at al. [1] suggested that the esterification of acrylic acid with *n*-butanol in the presence of heteropolyacid $H_3PW_{12}O_{40}$ is a second-order reaction. However, their experimental data are scarce and limited only to the temperature of 353 K.

The present study aims to determine the kinetics of the esterification of acrylic acid with *n*-propanol and *n*-butanol over dodecatungstophosphoric acid ($H_3PW_{12}O_{40}$) and dodecamolybdophosphoric acid ($H_3PMo_{12}O_{40}$) as catalysts.

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## EXPERIMENTAL

Kinetic experiments were carried out in a typical batch reactor of 100-mL capacity, which was mechanically agitated with an impeller and fitted with a reflux condenser. The temperature was maintained within ±0.5°C. The mixing speed of about 1000 rpm was determined to be sufficient to eliminate any mass transfer limitation. No change in the reaction rate was detected when the stirrer speed was varied from 550 to 1500 rpm. To initiate an experimental run, a known amount of alcohol was charged to the reactor and heated to the desired temperature. Acrylic acid was added at the desired mole ratio. Next, the catalyst $H_3PW_{12}O_{40}$ or $H_3PMo_{12}O_{40}$ was introduced to the reaction medium. To avoid side reactions of polymerization, hydroquinone was added to the reactor. Chromatography revealed that the reaction mixture contained mostly the products of esterification (ester and water) and only trace amounts of the products of side reactions. Therefore, it was possible to check the progress of the reaction by determining the acidity of the reaction system. The acid number was established through the titration of KOH samples. Samples of the reaction mixture were immediately diluted in cold 2-propanol, and reaction stopped because of cooling and dilution. The duration of the process and the frequency of sampling were selected for individual experiments, depending on the conditions of the reaction. The experiments were conducted till the moment when minimal changes in the concentrations of the reactants were noticed.

The molar ratio of alcohol to acid at the beginning of the reaction was 3:1, 5:1, and 10:1. The catalyst concentrations were 1.23, 2.95, 4.92, and 9.84 wt% for dodecatungstophosphoric acid and 3.12, 6.24, and 12.48 wt% for dodecamolybdophosphoric acid. The experiments were carried out at several temperatures from 318 to 368 K for *n*-propanol and from 343 to 373 K for *n*-butanol.

## RESULTS

The esterification of acrylic acid with aliphatic alcohol is a typical reversible reaction described by the following equation:

$$H_2C{=}CH{-}COOH + R'OH \Leftrightarrow H_2C{=}CHCOOR' + H_2O \tag{1}$$

Based on the stoichiometric equation, an extended kinetic equation, in which acrylic acid is a reference reactant, can be written in the following form:

$$r_K = k_1\left(c_K^a c_A^b - \frac{c_E^c c_W^d}{K_a}\right) \tag{2}$$

where $K$ and $A$ refer to acrylic acid and alcohol, respectively, and $W$ and $E$ refer to water and one of the possible esters, respectively.

Then, using the mass balance of the reference constituent in a batch reactor (assuming a constant density), the following relation is obtained:

$$-\frac{\mathrm{d}c_K}{\mathrm{d}t} = k_1\left(c_K^a c_A^b - \frac{c_E^c c_W^d}{K_a}\right) \tag{3}$$

If the actual concentration of acrylic acid is represented by its initial concentration, $C_{K_0}$, and degree of conversion, $\alpha_K$, Eq. (3) can be written as follows:

$$\frac{\mathrm{d}\alpha_K}{\mathrm{d}t} = c_{K_0}^{(a+b-1)} k_1\left((1-\alpha_K)^a\left(\frac{n_{A_0}}{n_{K_0}} - \alpha_K\right)^b - c_{K_0}^{c+d-a-b}\frac{\left(\alpha_K^{(c+d)}\right)}{K_a}\right) \tag{4}$$

where $n_{A_0}$ and $n_{K_0}$ are the initial numbers of moles.

By integrating Eq. (4) for the different values of exponents assumed, we tried to find a solution that

**Table I** The Estimated Activity Coefficients for *n*-Butanol at a Temperature of 363 K and the Initial Molar Ratio of Acrylic Acid to Alcohol of 1:3

| $x_K$ | $x_A$ | $x_E$ | $x_W$ | $\gamma_K$ | $\gamma_A$ | $\gamma_E$ | $\gamma_W$ |
|---|---|---|---|---|---|---|---|
| 0.225 | 0.725 | 0.025 | 0.025 | 0.932 | 1.006 | 1.967 | 2.823 |
| 0.200 | 0.700 | 0.050 | 0.050 | 0.899 | 1.018 | 1.922 | 2.833 |
| 0.175 | 0.675 | 0.075 | 0.075 | 0.866 | 1.030 | 1.879 | 2.841 |
| 0.150 | 0.650 | 0.100 | 0.100 | 0.835 | 1.042 | 1.836 | 2.848 |
| 0.125 | 0.625 | 0.125 | 0.125 | 0.805 | 1.055 | 1.793 | 2.853 |
| 0.100 | 0.600 | 0.150 | 0.150 | 0.776 | 1.067 | 1.751 | 2.858 |
| 0.075 | 0.575 | 0.175 | 0.175 | 0.748 | 1.080 | 1.710 | 2.861 |
| 0.050 | 0.550 | 0.200 | 0.200 | 0.720 | 1.092 | 1.670 | 2.864 |
| 0.025 | 0.525 | 0.225 | 0.225 | 0.694 | 1.105 | 1.630 | 2.866 |

**Table II** Calculated Values of the Equilibrium Constants and Equilibrium Degree of Conversions of Acrylic Acid at Various Temperatures

| $T$ | $\alpha^*$ | $n_{A0}/n_{B0}$ | $K_x$ | $K\gamma$ | $K_a$ |
|---|---|---|---|---|---|
| $n$-Propanol | | | | | |
| 318 | 0.775 | 1:3 | 1.20 | 5.70 | 6.87 |
| 328 | 0.811 | 1:3 | 1.59 | 5.66 | 9.00 |
| 338 | 0.831 | 1:3 | 1.88 | 5.57 | 10.48 |
| 348 | 0.849 | 1:3 | 2.22 | 5.48 | 12.17 |
| 358 | 0.866 | 1:3 | 2.61 | 5.39 | 14.07 |
| $n$-Butanol | | | | | |
| 343 | 0.905 | 1:3 | 2.10 | 7.50 | 15.74 |
| 353 | 0.925 | 1:3 | 2.80 | 7.36 | 20.62 |
| 363 | 0.955 | 1:3 | 4.00 | 7.23 | 28.93 |

would ensure the best fit between the reaction rate equation and the experimental data. To do so, we used a numerical integration method.

$$k_1 t = c_{K_0}^{(a+b-1)} \int_0^{\alpha_K} \frac{\mathrm{d}\alpha_K}{\left((1-\alpha_K)^a \left(\frac{n_{A_0}}{n_{K_0}} - \alpha_K\right)^b - c_{K_0}^{c+d-a-b} \frac{\left(\alpha_K^{(c+d)}\right)}{K_a}\right)} = \Phi(\alpha_K) \qquad (5)$$

Our numerous calculations showed that a linear relationship $\Phi(\alpha_K) = k_1 t$ in the coordinate system ($t$, $\Phi$) was difficult to reach, and the model obtained gave major errors. Since the chemical reactions under study took place in the liquid state and the reactants formed a multicomponent mixture of polar substances, we determined their activity coefficients. The determination was made by the UNIFAC method, and the necessary data were derived from [2]. Table I shows examples of activity coefficients for the reaction of acrylic acid with butanol at a constant temperature. Because the order of the values obtained for the other reactions at various temperatures was similar, we inferred that the reaction rate was proportional to the activity rather than the concentration of the reactants. Therefore, the kinetic model was expressed in terms of both the activities and molar concentrations. Because the reaction system was better described when, was assumed to be nonideal of the liquid mixture, we replace the concentration of the reactants in Eq. (2) with their activities. Then, using the mass balance we obtained the relation

$$-\frac{\mathrm{d}c_K}{\mathrm{d}t} = k_1\left(\gamma_K^a c_K^a \gamma_A^b c_A^b - \frac{\gamma_E^c c_E^c \gamma_W^d c_W^d}{K_a}\right) \qquad (6)$$

where $\gamma$ is the activity coefficient of the component.

The differential equations (3) and (6) after transformation were integrated numerically by the Simson's method.

Using the equilibrium degrees of conversion, determined on the basis of the acrylic acid concentration established experimentally in the state of equilibrium,

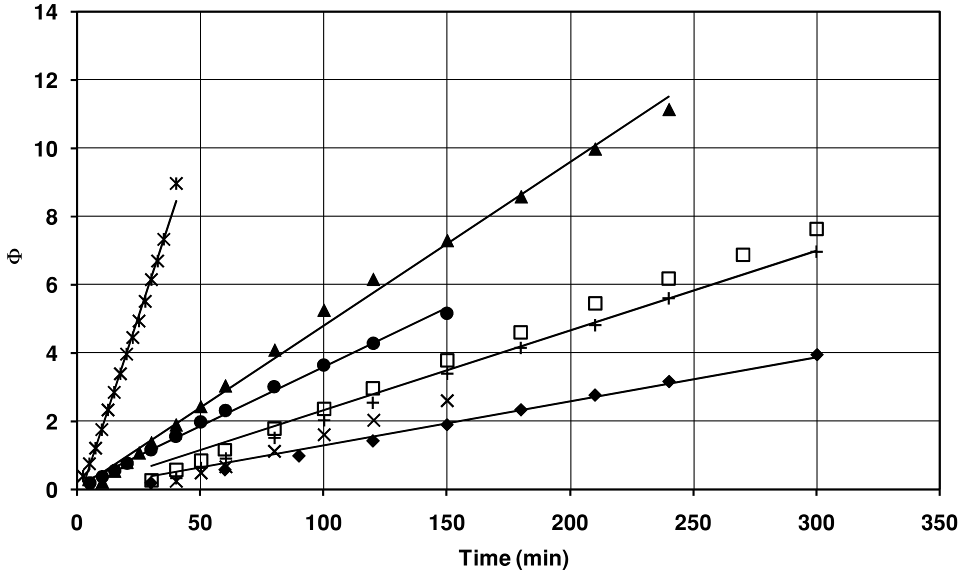

**Figure 1** Model fitting for the esterification of acrylic acid with $n$-propanol in the presence of $H_3PW_{12}O_{40}$ (♦: $T = 348$ K 1:3 catalyst 4.92 wt%, □: $T = 358$ K 1:3 catalyst 4.92 wt%, +: $T = 358$ K 1:5 catalyst 4.92 wt%, ×: $T = 358$ K 1:10 catalyst 4.92 wt%. ●: $T = 358$ K 1:3 catalyst 2.95 wt%, ▲: $T = 368$ K 1:3 catalyst 4.92 wt%, ∗: $T = 358$ K 1:3 catalyst 9.84 wt%).

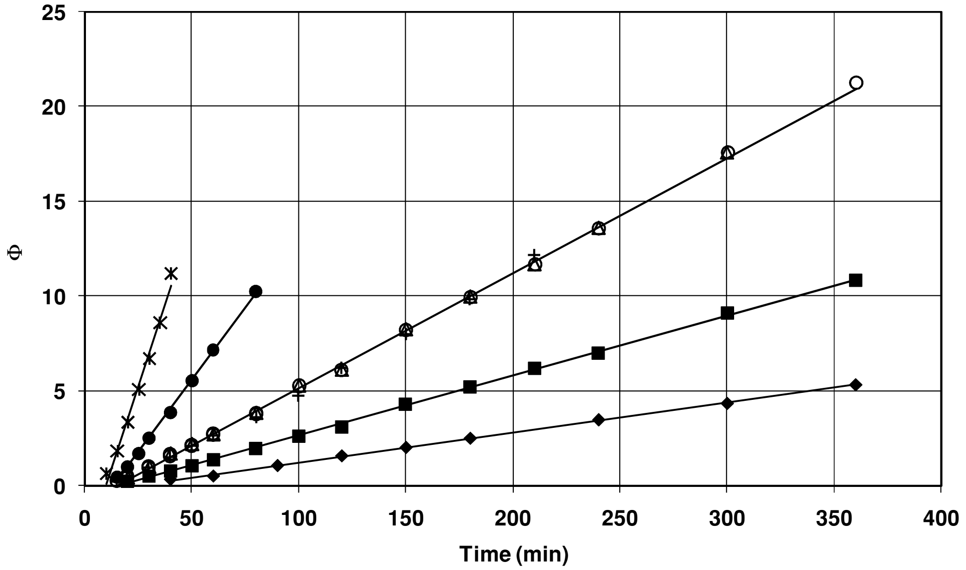

**Figure 2** Model fitting for the esterification of acrylic acid with *n*-propanol in the presence of $H_3PMo_{12}O_{40}$ (◆: $T = 348$ K 1:3 catalyst 3.12 wt%, ■: $T = 358$ K 1:3 catalyst 3.12 wt%, △: $T = 368$ K 1:3 catalyst 3.12 wt%, +: $T = 368$ K 1:5 catalyst 3.12 wt%, ○: $T = 368$ K 1:10 catalyst 3.12 wt%, ●: $T = 368$ K 1:5 catalyst 6.24 wt%, ∗: $T = 368$ K 1:5 catalyst 12.48 wt%).

we determined the thermodynamic equilibrium constants $K_a$ from the following equation:

$$K_a = \left(\frac{a_E a_W}{a_K a_A}\right)_{\text{eq}} = \left(\frac{x_E x_W}{x_K x_A}\right)_{\text{eq}} \left(\frac{\gamma_E \gamma_W}{\gamma_K \gamma_A}\right)_{\text{eq}} \qquad (7)$$

where $a$ is the activity of the component and $x$ is the molar fraction of the component.

Table II shows the values of the equilibrium degrees of conversion for propanol and butanol and the values of the constants at various temperatures. The equilibrium constant was expressed as a function of temperature as follows:

$$n\text{-propanol} \quad K_a = 3.630 \times 10^3 \exp\left(\frac{-16700}{RT}\right) \qquad (8)$$

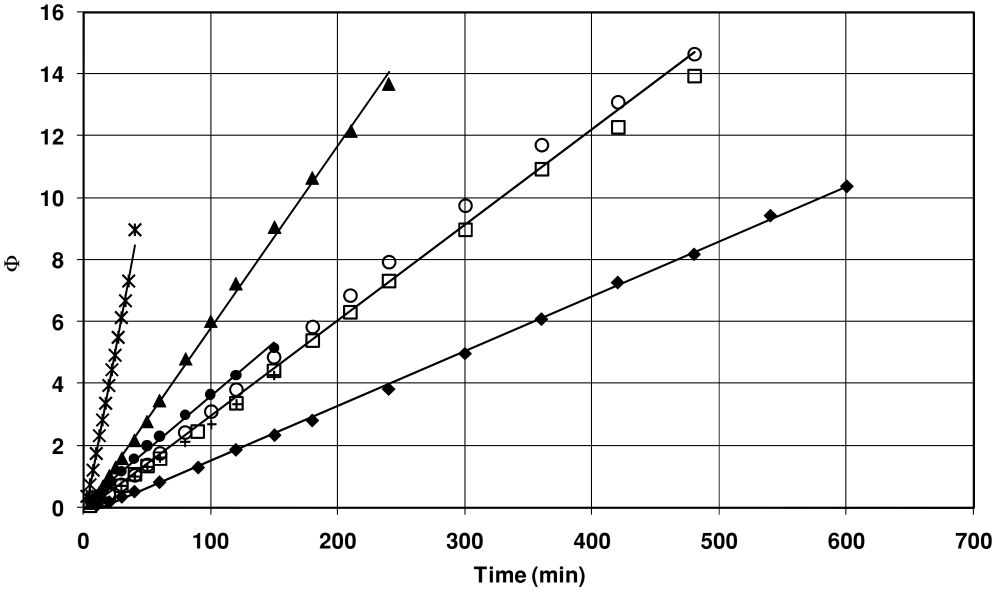

**Figure 3** Model fitting for the esterification of acrylic acid with *n*-butanol in the presence of $H_3PW_{12}O_{40}$ (◆: $T = 353$ K 1:3 catalyst 2.95 wt%, ○: $T = 363$ K 1:3 catalyst 2.95 wt%, □: $T = 363$ K 1:5 catalyst 2.95 wt%, +: $T = 363$ K 1:10 catalyst 2.95 wt%, ●: $T = 363$ K 1:3 catalyst 1.23 wt%, ▲: $T = 373$ K 1:3 catalyst 2.95 wt%, ∗: $T = 363$ K 1:3 catalyst 4.92 wt%).

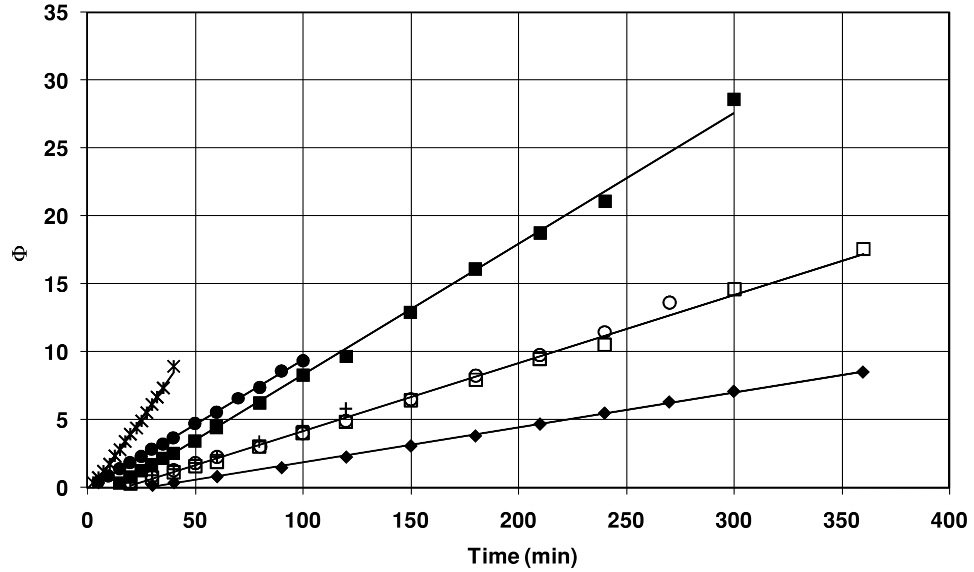

**Figure 4** Model fitting for the esterification of acrylic acid with *n*-butanol in the presence of $H_3PMo_{12}O_{40}$ (♦: $T = 353$ K 1:3 catalyst 3.12 wt%, ○: $T = 363$ K 1:3 catalyst 3.12 wt%, □: $T = 363$ K 1:5 catalyst 3.12 wt%, +: $T = 363$ K 1:10 catalyst 3.12 wt%, ■: $T = 373$ K 1:3 catalyst 3.12 wt%, ●: $T = 363$ K 1:5 catalyst 6.24 wt%, ∗: $T = 363$ K 1:5 catalyst 12.48 wt%).

$$n\text{-butanol} \quad K_a = 9.603 \times 10^5 \exp\left(\frac{-31400}{RT}\right) \tag{9}$$

We observed that temperature had a stronger effect on chemical equilibrium in the case of the butyl acrylate synthesis.

Finally, using Eq. (6), we obtained (in all cases) a nonelementary form of the kinetic equation:

$$r_K = k_1 \times c_{\text{cat}}\left(\frac{a_K a_A}{a_E^{0.5}} - \frac{a_E^{0.5} a_W}{K_a}\right) \tag{10}$$

Figures 1–4 show the graphs of the function $\Phi(\alpha_K) = k_1 t$ in the coordinate system $(t, \Phi)$. As the experimental points in the graphs were scattered around a straight line, we assumed that the adopted form of the kinetic equation was correct. The determining criterion for the form of the equation was the graph of the function $\Phi(\alpha_K) = k_1 t$ for experiments conducted at the same temperature but at different initial molar ratios of alcohol to acrylic acid.

The reaction rate constant was related to the temperature using the Arrhenius equation:

$$k_1 = k_0 \exp\left(\frac{-E}{RT}\right) \tag{11}$$

Table III shows the values of the frequency factor $k_0$ and the energy of activation $E$ established by a linear regression.

**Table III** Kinetic Parameters

| Catalyst | $E$(J mol$^{-1}$) | $k_0$ (m$^{4.5}$ mol$^{-1.5}$ min$^{-1}$) |
|---|---|---|
| *n*-Propanol | | |
| $H_3PW_{12}O_{40}$ | 65,200 ± 600 | $6.08 \times 10^3$ |
| $H_3PMo_{12}O_{40}$ | 69,400 ± 1000 | $3.26 \times 10^4$ |
| *n*-Butanol | | |
| $H_3PW_{12}O_{40}$ | 66,000 ± 400 | $1.12 \times 10^4$ |
| $H_3PMo_{12}O_{40}$ | 72,300 ± 800 | $9.82 \times 10^4$ |

**Table IV** Time Needed to Reach the Degree of Conversion of 0.6 at a Temperature of 363 K (the Initial Molar Ratio of Acrylic Acid to Alcohol of 1:3 and the Catalyst Concentration of 15 mol m$^{-3}$)

| | Time (min) | |
|---|---|---|
| | $H_3PW_{12}O_{40}$ | $H_3PMo_{12}O_{40}$ |
| *n*-Propanol | 166 | 130 |
| *n*-Butanol | 128 | 120 |

## CONCLUSIONS

The results of our extensive research provided the basis for working out kinetic equations and determining the values of constants appearing in the equations.

As indicated by the catalytic activities of the heteropolyacids under study, dodecamolybdophosphoric acid was more active than dodecatungstophosphoric acid both for *n*-propanol and *n*-butanol (Table IV). The time needed to reach the degree of conversion 0.6 for the reactions carried out in the presence of both catalysts was shorter for *n*-butanol (Table IV), which suggests that this reaction proceeded faster.

Comparison of the kinetic models of the heteropolyacid-catalyzed reactions under study with those of the reactions catalyzed by commonly used sulfuric acid leads to some noteworthy conclusions. The form of the kinetic equation for the latter depended on the length of the carbon chain in the alcohol molecule: for *n*-butanol [3] and higher alcohols [4] the kinetics was elementary, whereas for *n*-propanol [3] and lower alcohols [5] the reaction was fourth order (second order in acid and alcohol for esterification, and second order in ester and water for hydrolysis). In contrast, for heteropolyacids in this study the kinetic equation in all cases had a nonelementary form.

## BIBLIOGRAPHY

1. Chen, X.; Xu, Z.; Okuhara, T. Appl Catal 1999, 180, 261–269.
2. Hansen, H.; Rasmussen, P.; Fredenslund, A.; Schiller, M.; Gmehling, J. Ind Eng Chem Res 1991, 30, 2352–2355.
3. Grzesik, M.; Skrzypek, J.; Witczak, M. Stud Surface Sci Catal 1999, 122, 415–418.
4. Grzesik, M.; Skrzypek, J.; Witczak, M. Przem Chem 2000, 79, 271–273.
5. Witczak, M.; Grzesik, M.; Skrzypek, J. Inż Chem Proc 2004, 25, 331–340.