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ORIGINAL RESEARCH PAPER

SYNTHESIS OF ACRYLIC ESTERS IN PHASE TRANSFER CATALYSIS: KINETICS AND ECOLOGICAL ASPECTS

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Abstract: Phase-Transfer Catalysis (PTC) technology is used in the commercial manufacture and also in pollution mitigation treatment processes. In the paper is demonstrated the synthesis of esters of acrylic and metacrylic acids, which have wide applications in the industry for the synthesis of unique polymeric materials, by phase transfer catalysis method. It is necessary to notice that the synthesis of acrylic acids in PTC medium is more important because that compounds are more sensitive at acidic and basic conditions.
Here is shown that the offered method has more advantages in comparison with the traditional methods. PTC is characterized by a higher degree of conversion of raw materials into useful products, smaller material and power resources consumption.
The offered method for acrylic ester synthesis in comparison with the traditional methods has more advantages: higher process rates, mild reaction conditions, allowing lower energy costs, the complete elimination of hazardous and dangerous organic solvents, all leading to a sharp reduction of air pollution, and volume of generated wastewaters.

Keywords: *acrylic acid, acrylic ester, alkyl halide, environmental protection, kinetic characteristic, phase transfer catalysis*

INTRODUCTION

In the processes of chemical technology, as a rule, there are a lot of stages and manufactures, which can be supplemented by various stages of recycling processes.
Phase transfer catalysis (PTC) due to the advantages, has wide application in the industry of organic synthesis [1, 2]. From the standpoint of the process chemist PTC having the advantages of being a proven technology involving simple and easily evaluated procedures with high yield (often > 90%) and increased reaction rates, sometimes leading to enhanced selectivity [2]. As one of major tasks facing by a chemical industry is the development and realization of necessary measures for exception of harmful influence of the enterprises on an environment, translation on few waste technology, PTC correspond perfectly to these criteria - the ability to use NaOH as a base instead of more expensive and hazardous organic bases, viability in the water in presence of water and avoidance of run-away conditions. PTC technology is also used in pollution prevention, pollution treatment and the removal or destruction of impurities in waste and product streams [2].
In our group it has been showed an opportunity of synthesis of ethers and esters in PTC conditions [3 – 5]. These investigations have allowed to develop the synthesis of unsaturated ethers (as allyl furfuryl, propargyl furfuryl ethers, and esters of acrylic and methacrylic acids), which have wide application in industry for the synthesis of unique polymeric materials [6]. Furfuryl ethers and esters were used also for intramolecular Diels-Alder reaction [4].

$$CH_2{=}CX{-}COOH + RHal \longrightarrow CH_2{=}CX{-}COOR + HHal$$

X = H, CH_3
R = alkyl, alkenyl, furfuryl
Hal = Cl, Br

This reaction was carried out in aqueous phase, there acrylic acid is stable [7]. But, it iss known that reaction systems that lack an aqueous phase are very attractive to chemists. Therefore, we have tried to carry out the reaction with smaller amount of water (10 N), thus having solved also the ecological task. We hope that the proposal synthesis of acrylic esters will give the chance for a choice of optimum variants environmental friendly technology by comparison with existing processes.

EXPERIMENTAL

Synthesis

The synthesis of acrylic esters is carried out by interaction of acrylic acid with alkyl halides in the presence of the sodium hydroxide (or KOH) in aqueous solution, the catalytic amounts of quaternary ammonium salts [catamin AB – the mixture of NN-dimethyl-N-benzyl-N-alkyl (C_{12}-C_{18}) ammonium chlorides, industrial SAC], hydroquinone, at the temperature 55 – 75°C during 1 – 1½ hours. The molar ratio of acid : alkyl halide : sodium hydroxide : quaternary ammonium salts – is 1 : 1.2 : 1,0 : 0.1. The amount of hydroquinone is 0.5 gram for 0.5 mol acid. The simplicity of

performance and the higher yields (75 – 90%) of target products can predetermine the application of the present method in industry.

Acrylic acid benzyl ester

It has been placed in flask 3.6g (0.05 mol) acrylic acid, 5mL 10N of a NaOH aqueous solution, 0.7g (0.001 mol) catamin-AB as 50% water solution and 0.05 g hydroquinone. At room temperature (18°C) on drops of 7.6 g (0.06 mol) benzylchloride was added during 20 min. A mix heated up to 75°C and continued hashing 40 min.

Then a reactionary mix cooled and extracted three times by ether (totally 100 mL) and dried up above anhydrous Na_2SO_4. After removal of the ether the product was overtaken under vacuum, received 7.3 g (90% yield) benzyl acrylate, b.p.114 – 117°C / 7 mm, N^{20}_D = 1.5243) [7].

IR, ν, cm^{-1}: 700, 750, 1490, 1590, 1625, 1725, 3030, 3060, 3090.

NMR: 5.06s (CH_2), 5.50 – 6.37m ($CH=CH_2$), 7.11m (C_6H_5).

The same processes were performed for the preparation of furfurylic ester of acrylic acid.

Acrylic acid allyl ester

Similarly above mentioned conditions from 3.6 g (0.05 mol) acrylic acid, 5 mL 10N of an aqueous solution of NaOH, 0.7 g (0.001 mol) catamin-AB as 50% water solution, 0.05 g hydroquinone and 7.26g (0.06 mol) allyl bromide has been received 5.11g (91% yield) allyl acrylate, b.p. 119 – 120°C / 680 mm, N^{20}_D = 1.4335 [7].

Acrylic acid n-amyl ester

Similarly above mentioned conditions from 3.6 g (0.05 mol) acrylic acid, 5 mL 10N of an aqueous solution of NaOH, 0.7 g (0.001 mol) catamin-AB as 50% water solution, 0.05 g hydroquinone and 9.1 g (0.06 mol) *n*-amyl bromide has been received 5 g (70% yield) *n*-amyl acrylate, b.p. 53 - 54°C / 9 mm, N^{20}_D = 1.4240 [7].

Acrylic acid glycidyl ester

Similarly above mentioned conditions from 3.6 g (0.05 mol) acrylic acid, 5 mL 10N of an aqueous solution of NaOH, 0.7 g (0.001 mol) catamin-AB as 50% water solution, 0.05 g hydroquinone and 5.55 g (0.06 mol) epychlorhydrin has been received 4.38 g (70% yield) glycidylacrylate, b.p. 162 – 163°C / 80 mm, N^{20}_D = 1,4820 [7].

IR, ν, cm^{-1}: 1725.

NMR: 1.60 – 1.68 m (3H, $CH-CH_2$), 4.21t (2H, OCH_2), 5.65 – 6.35m (3H, $CH=CH_2$).

Metacrylic acid n-butyl ester

Similarly above mentioned conditions from 4.3 g (0.05 mol) metacrylic acid, 5 mL 10N of an aqueous solution of NaOH, 0.7 g (0.001 mol) catamin-AB as 50% water solution, 0.05 g hydroquinone and 8.22 g (0.06 mol) *n*-butyl bromide has been received 3.9 g (55% yield) *n*-butyl metacrylate, b.p. 60 – 61°C / 12 mm, N^{20}_D = 1.4256 [7].

Kinetics

We carry out also the definition of kinetic characteristics of the synthesis of more interesting monomer - allyl acrylate. The reaction mixture was heated up to necessary

temperature, which was kept up constant during 1 hour. The tests were selected on the analysis every 10 minutes (Figure 1). The reaction temperature was varied in the limits of 25 – 65°C. Activation energy (E) and k_o were graphically determined from Arrhenius coordinates:

E = 55625 kJ/kmol (13.28 kcal/mol)

$k_o = 1.922\times10^7$ m$^{3.078}$ (kmol$^{1.026}$ min)

It had been established that the reaction kinetic of acrylic acid with allyl bromide in PTC conditions can be described by the equation:

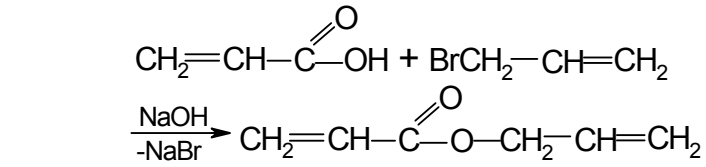
$$-\frac{dC_a}{d\tau} = k \cdot C_A^{1.975} \cdot C_B^{0.051}$$

where:

$$k = 1.922\times10^7 \exp\left(-\frac{55625}{8.314T}\right);$$

C_A - concentration of acrylic acid;

C_B - concentration of allyl bromide.



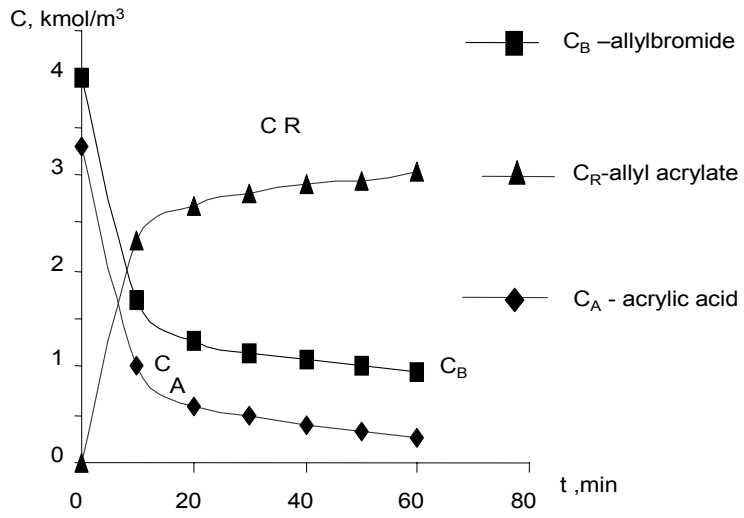


Figure 1. *The kinetic curves of the charge initial substances and accumulation of a product of reaction at the synthesis of allyl acrylate at T = 65°C*

RESULTS AND DISCUSSION

The preparation of acrylic esters is an important synthetic reaction for which a variety of procedures have been developed during the last 50 – 60 years [7]. In traditionally the

esters receive by interaction of carbonic acids with the alcohols in the presence of strong acids at higher temperature: 105 – 121°C [7], an argon current at 90°C [8], and long duration of reaction (55 – 60 h) at 20 – 25°C [9]. The symmetric ether is formed also from the appropriate alcohol in acidic medium, which creates difficulties at allocation of a desirable product [8]. It is necessary to note, that in case of the excess of alkali (it is usual in alkylation reaction in PTC conditions to double the excess of alkali) the yield of an ester usually falls [3]. On all probability, the reaction of hydrolysis of an ester takes place.

In reaction condition was formed other by-product as the derivative of propanoic acid [10]. The strong acidic conditions environmentally are less preferable than the basic conditions [11].

Besides, as a rule, because of convertibility of process in acidic medium it is rather difficult to reach high yields of desirable product and requires also additional expenses of neutralization of a reactionary mix by alkali materials [12]. Such technology differs by complexity and huge equipment with the difficulties of its operation. The ion exchange materials are expensive, quickly fail, require difficult regeneration, during which huge amounts of wastewater is formed [13]. Other method of this ester synthesis is the interaction of alkyl halogen or other esters with the acrylic acid salts in the presence of organic solvents (acetonitrile, dimethylformamide and other expensive, hazardous and fire-explosive solvents). The toxicity of this solvents in atmosphere within the limits of 10 mg/m^3, their receipt in organism results in a sharp poisoning – is observed initial, narcotic action or excitation, frustration of coordination, spasm infringement of breath.

Received kinetic equation allows us to determine optimum parameters of synthesis acrylic esters for account the simple hashing type reactor.

The greatest disadvantage of acrylic esters synthesis from salts is the preparation of metal salts under anhydrous conditions [1, 2]. Acrylic acid is converted into organic salts by the reaction with sodium or sodium hydride. The use of PTC to synthesize acrylic esthers improves the conventional methods. PTC has the advantage that the acrylic salt is synthesized *in situ* directly by the reaction of acid with alkaline solution in the aqueous solution. The final product is readily removed from the organic solvent simply by evaporation of the solvent.

The solvent in our case is not applied, as an organic phase enters itself. The quantity of used water is also reduced.

The reaction has appeared of the second order under the relation of acrylic acid, and zero - in relation to allyl bromide. Received equation allows calculating optimum parameters of process and reactor of ideal mixture for the synthesis of allyl acrylate.

The kinetics of the described synthesis of allyl acrylate testifies for the benefit of the PTC mechanism. Really, the order of reaction for allyl acrylate $\alpha_B = 0.051$ (i.e. very close to zero) speaks that the process is supervised on the diffusion of acrylate ions from a water phase in organic, which is consist only from allyl bromide. The rather quantity of energy of activation also is determined by the contribution of the diffusion factor.

The synthesis of acrylic esters carry out in multi section apparatus, filled by strong acidic ion exchangers.

Received kinetic equation allows us to determine optimum parameters of synthesis acrylic esters for account the simple hashing type reactor.

CONCLUSIONS

Procedures based on PTC in the substitutions usually excel over traditional methods owing to their simplicity, high yields and quality of final products. This method is especially valuable for reaction with compounds sensitive to water.
The offered method for acrylic ester synthesis in comparison with the traditional methods has more advantages: high speed of process, soft condition of reaction allowing lowering of the power expenses, the complete exception of application of hazardous and dangerous organic solvents, by virtue of – it is sharp reduction of air pollution, much smaller volumes of waste water. It should be note that the in offered synthesis of acrylates the alkylating agent – allyl bromide use completely. All of this is devoted to technological problems of the synthesis of ethers in the aspect of the environmental protection.

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