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Esterification of Dicarboxylic Acids with Benzyl Alcohol under the Action of the Microwave Radiation

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Abstract—Reaction of dicarboxylic acid with benzyl alcohol under the microwave irradiation proceeds faster as compared to the thermal conditions. The main reaction products are alkyl dicarboxylates, and the monoester and dibenzyl ether are formed as the side products. A proposal about the nature of the nonthermal effect in the reactions stimulated by the microwave irradiation is considered.

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Intensification of chemical processes by the application of microwave irradiation is an important method of the energy saving technologies. This method of activation is used successfully for performing a wide range of chemical processes [1–4]. The thermal and specific (nonthermal) effects of the microwave activation of chemical processes are distinguished [5, 6]. In the first case the rates of chemical reactions under the conditions of the microwave heating are equal to the rates of thermal reactions when the temperatures of the reaction mixtures are the same. In the second case the micriwave-stimulated reactions proceed significantly faster than the thermal ones. Specific effect of the microwave irradiation presents a great interest because it permits to increase the reaction rate without the introduction of catalysts.

Alkyl carboxylates are important products of the industrial organic chemistry. They are widely used as the plasticizers of the polymeric materials, unsaturated polyesters are used for preparation of polyester resins and serve also as the starting products in the synthesis of polyurethanes. Microwave irradiation is an effective tool for the stimulation of esterification of carboxylic acids with alcohols. For example the almost quantitative esterification of acetic and benzoic acids with higher alcohols in the presence of heteropolyacids under the conditions of the microwave irradiation has been reported [7].

A successful industrial examination of a pilot flow-type plant for esterification of monocarboxylic acids with alcohols in the presence of alumosilicates under the microwave irradiation heating has also been reported [8].

Effect of the microwave radiation on the esterification of carboxylic acids is not unambiguous. No specific effect was found during the esterification of propionic acid with propanol-1 [5] and of benzoic acid with ethanol [9]. In both cases the microwave irradiation was only a means for the heating the reaction mixture. At the same time esterification of benzoic acid with metanol [10] and of metacrylic acid with phenol [11] demonstrated clear specific effect. Thermal polycondensation of lactic acid does not take place at 200°C, but it proceeds successfully at the same temperature under the microwave irradiation [12].

Reported data on the esterification of carboxylic acids under the action of microwave irradiation deal mainly with monobasic acids, while the reports on esterification of dibasic acids are scarce [13]. At the same time dicarboxylic acid esters have important practical use.

With the purpose of revealing the rules of formation of the dicarboxylic acid esters under the microwave irradiation of reaction mixtures we studied esterification of a series of dicarboxylic acids with benzyl alcohol.

$$\underset{\textbf{Ia–Ig}}{\mathrm{HOOC{-}R{-}COOH}} + \underset{\textbf{II}}{\mathrm{HOCH_2C_6H_5}} \xrightarrow[-\mathrm{H_2O}]{} \underset{\textbf{IIIa–IIIg}}{\mathrm{HOOC{-}R{-}COOCH_2C_6H_5}}$$

$$\underset{\textbf{IIIa–IIIg}}{\mathrm{HOOC{-}R{-}COOCH_2C_6H_5}} + \underset{\textbf{II}}{\mathrm{HOCH_2C_6H_5}} \xrightarrow[-\mathrm{H_2O}]{} \underset{\textbf{IVa–IVg}}{\mathrm{C_6H_5CH_2OCO{-}R{-}COOCH_2C_6H_5}}$$

R = $-(CH_2)_2-$ (**a**), $-(CH_2)_3-$ (**b**), $-(CH_2)_4-$ (**c**), $-(CH_2)_6-$ (**d**), $-(CH_2)_7-$ (**e**), $-(CH_2)_8-$ (**f**), *trans*–CH=CH– (**g**).

The reaction under investigation is a two-stage process with the intermediate formation of acid monoesters **IIIa–IIIg**. Benzyl alcohol **II** was chosen by us as a high-boiling compound, convenient for the investigation of the transformations with its participation under the conditions of microwave irradiation.

In the first step of our studies we tried to reveal a non-thermal microwave effect on the esterification of dicarboxylic acids. With this purpose we carried out comparative investigation of carboxylic group consumption in the reaction of the acid **Ia** with the alcohol **II** under thermal conditions and microwave irradiation. The results obtained are presented in the Fig.1.

From the data presented follows that at the comparable temperature the thermal reaction proceeds significantly slower than the microwave-activated one. Hence, in the reaction under investigation the specific microwave effect is observed. From the fig.1 it follows that the acid number dependence on the reaction time under the microwave activation is linear. ^{1}H NMR studies of reaction mixtures showed that partial accumulation of water formed in the course of esterification takes place in the reaction mixture (Fig. 2). This should result in establishing of equilibrium between the reagents and the products.

In the course of the microwave-activated process a decrease in mass of the reaction mixture takes place (Fig. 3). This is caused by the evaporation of the benzyl alcohol–water azeotrope [14].

The data on the time dependence of the acid number in the microwave-activated reactions of the acids **Ia–Ig** with alcohol **II** are listed in Table 1. From these data follows that esterification of the acids **Ia–Ig** with the alcohol **II** proceeds in high yield. Besides the formation of the incomplete and complete esters **IIIa–IIIg**, **IVa–IVg** formation of dibenzyl ether **V** and of polycondensation product **VI** can take place.

$$2\,\textbf{II} \rightarrow \underset{\textbf{V}}{\mathrm{C_6H_5CH_2OCH_2C_6H_5}} + \mathrm{H_2O},$$

$$n\,\textbf{II} \rightarrow \underset{\textbf{VI}}{\mathrm{C_6H_5CH_2(C_6H_4CH_2)_{\mathit{n}-1}OH}} + (n-1)\,\mathrm{H_2O}.$$

These reactions are catalyzed by Brønsted acids [15]. With the purpose of establishing the selectivity of the microwave-activated esterification, a chromato-

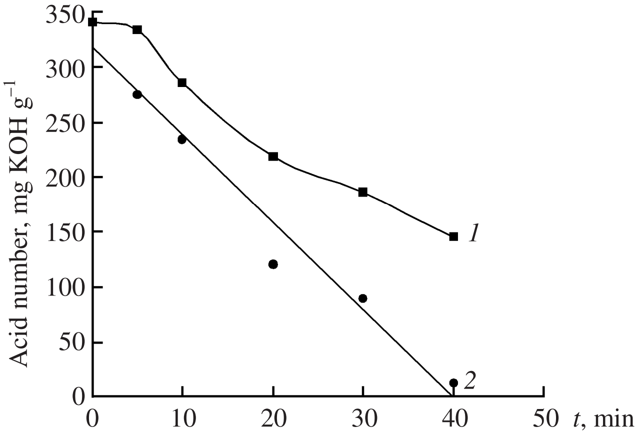

Fig. 1. Time (*t*) dependence of the acid number at the reaction of acid **Ia** with alcohol **II** at (*1*) 180°C and (*2*)under the microwave irradiation.

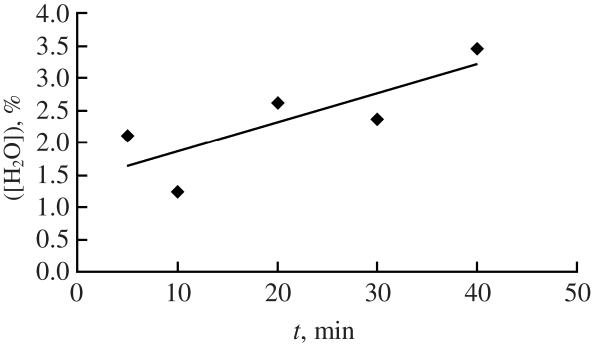

Fig. 2. Plot of water concentration ([H_2O]) against the reaction time (*t*) in the reaction of the acid **Ia** with the alcohol **II** under the conditions of microwave irradiation.

Table 1. Dependence of the acid number on time in the microwave-activated esterification of acids **Ia–Ig** with alcohol **II**

Compound	Acid number, mg KOH g^{-1}		
	initial	5 min	40 min
Ia	341	275	12.7
Ib	325	261	11.9
Ic	310	259	11.3
Id	283	277	9.35
Ie	278	246	9.7
If	255	247	9.4
Ig	388	340	4.6

Table 2. Composition of the reaction mixtures of acids **I** with alcohol **II** established by the chromato-mass spectrometric measurements

Reaction	Composition of the reaction mixture, wt %		
	III	**IV**	**V**
Ia + **II**	4.7	95.2	0.1
Ib + **II**	4.7	91.7	3.6
Id + **II**	4.4	93.2	2.4
Ig + **II**	1.6	95.9	2.5

mass spectrometric investigation of a series of crude reaction mixtures was carried out. The data obtained are listed in Table 2.

We found that in all the cases complete esters **IV** are the main reaction products. Content of the acid esters is insignificant. Formation of the by-product **V** was observed in all the cases, while no oligomer **VI** was found. Amount of the admixtures is too small that to be rgistered by the method of ^{1}H NMR spectroscopy.

Hence, the above-described studies show that the microwave-activated esterification of dicarboxylic acids is a convenient procedure for preparing their complete esters. Under these conditions the reaction proceeds faster than under the thermal activation. From that it follows that the specific microwave effect is observed. This effect has been discussed about, and some workers even reject its existence [16]. In this connection we want to note the following two curcumbstances.

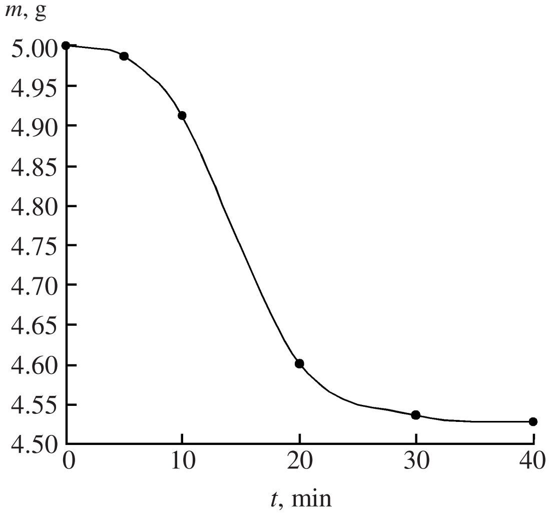

Fig. 3. Dependence the mass (m) of the reaction mixture on the reaction duration (t) at the microwave-activated esterification of acid **Ia** with alcohol **II**.

At first, the microwave-activated reactions are often carried out in the thermostable glass vessels. This material absorbs strongly in this spectral range. Due to that in the course of chemical transformations only the thermal effect of microwave activation is mainly observed because the reaction mixture is to a great extent is heated by the wall of the vessel. Teflon and quartz glass are more suitable materials for such apparatus because they do not practically absorb the microwave radiation.

The second statement is that the microwave radiation energy is consumed for excitation of the rotation levels of molecules. Such levels in turn are formed by the splitting of the vibrational levels. From this point of view excitation of the rotation levels must be always accompanied by partial excitation of the vibrational ones. In the course of chemical reaction the reacting system is transfered from the vibrational levels of the reagents onto the vibrational levels of the transition state. If the microwave radiation leads to diminishing in the energy difference of these two vibrational levels then the specific microwave effect becomes inevitable.

EXPERIMENTAL

^{1}H NMR spectra were taken on a Bruker DPX-400 spectrometer (400 MHz). DMSO-d_6 was used as a solvent and as the reference substance.

Chromatomass spectrometric studies were carried out on a Perkin-Elmer (Precisely) Clarus 500 mass spectrometer equipped with a MSD detector. The evaporator temperature 260°C, the initial column temperature 100°C. After 50 seconds the column temperature was elevated to 220°C at a rate of 15°C/min. Then the column temperature was elevated to 306°C at a rate of 8°C/min. The device was equipped with a 25000×0.2 mm capillary column, Elite-17 MS stationary phase, helium carrier gas.

Commercial dicarboxylic acids **Ia–Ig** (Fluka) were used, the main substance content being above 99.0%. No additional purification was carried out.

Benzyl alcohol was purified by vacuum distillation according to [14]. Its physicochemical constants were in agreement with the reported data.

The reactions were carried out in a Panasonic NN-CT337W microwave apparatus, the output power 800 W, working frequency 2.45 GHz.

Typical synthetic procedure for preparing benzyl dicarboxylates was the following. A mixture of 0.014 mol of dicarboxylic acid and 0.03 mol of benzyl alcohol was placed to a 40 ml cylindrical Teflon flask, mixed thoroughly until the formation of a homogenous mixture and placed to the microwave furnace. The exposition time was varied from 5 to 40 min, the temperature of the reaction mixture was varied in the range 150–80°C.

Kinetic studies of the reaction of succinic acid **Ia** with benzyl alcohol **II** were carried out under the above-described conditions. The microwave furnace was switched off from time to time, a sample was taken from the Teflon reaction vessel, and then the process was continued. The carboxy group content (GOST 25210-82) in the sample was evaluated.

Crude reaction mixtures were exposed to the ^{1}H NMR studies, the esters **IV** and water were identified.

Compound IVa. ^{1}H NMR spectrum, δ, ppm: 2.66 s (4H, CH_2CH_2), 5.09 s (4H, OCH_2–Ph), 7.36 m (10H, aromatic protons).

Compound IVb. ^{1}H NMR spectrum, δ, ppm: 1.82 m (2*H*, CH_2), 2.41 m (4H, CH_2CH_2), 5.09 s (4H, OCH_2–Ph), 7.36 m (10H, aromatic protons).

Compound IVd, δ, ppm: 1.26 m (4H, CH_2CH_2), 1.53 m (4*H*, CH_2CH_2), 2.34 m (4H, CH_2CH_2), 5.09 s (4H, OCH_2–h), 7.36 m (10H, aromatic protons).

Compound Vg. ^{1}H NMR spectrum, δ, ppm: 5.24 s (4H, OCH_2–Ph), 6.86 s (2H, CH=CH), 7.39 m (4H, aromatic protons), 7.41 m (6H, aromatic protons).

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