Peculiarities of obtaining 2-hydroxyethyl-1,3,4-trimethylcyclohex-3-encarboxylate

I. S. Kostiv, G. O. Marshalok,

National University "Lviv Polytechnic," st. Bandery 12,
Lviv, 79013 Ukraine
E-mail: kostiv.irina@gmail.com

Abstract – The process of diene cyclization of 2,3-dimethylbutadiene with 2-hydroxyethylmethacrylate was investigated. Effects of temperature, reaction duration, and ratio of reagents on the yield of 2-hydroxyethyl-1,3,4-trimethylcyclohex-3-encarboxylate was studied. Optimal conditions of passing the process were found. Kinetic regularities of 2-hydroxyethyl-1,3,4-trimethylcyclohex-3-encarboxylate obtaining has been investigated. On the basis of the obtained results the optimal conditions of the target product synthesis have been established.

Key words – 2,3-dimethylbuta-1,3-diene, 2-hydroxy-ethylmethacrylate, 2-hydroxyethyl-1,3,4-trimethylcyclohex-3-encarboxylat, cycloaddition reaction.

I. Introduction

Alkylcyclohexene derivatives are interesting for research, since the presence of homologous series creates the feasibility for synthesis of secondary and tertiary hydroaromatic alcohols and hydroaromatic hydrocarbons. These compounds, *e.g.* alkylcyclohexenecarboxylates, are poorly studied, the processes of their obtaining described in literature mainly belong to the saturated derivatives of cyclohexencarboxylates. Alkylcyclohexenecarboxylates are used in production of such cosmetics as lotions, body emulsions, shampoos, day and night creams [1, 2]. They are valuable raw materials for the perfume compositions, because they have the pleasant floral, citrus and refreshing scents [3]. Optical lenses are received by alkylcyclohexenecarboxylates polymerisation.

The aim of this work was the extension of the assortment of esters of cyclohexenecarboxylic acids due to obtaining new monomers, unsaturated esters of alkylsubstutited cyclohexenecarboxylic acids. In this work kinetics of 2-hydroxyethyl-1,3,4-trimethylcyclohex-3-encarboxylate obtaining was investigated and optimal conditions for its synthesis using the Diels-Alder reaction were established.

II. Experiment

2-Hydroxyethyl-1,3,4-trimethylcyclohex-3-encarboxylate (HTMC) was synthesized by us for the first time using 2-hydroxyethylmethacrylate (HEMA) 2,3-dimethylbutadiene (DMB). For synthesis we used 2-hydroxyethylmethacrylate mark "c.p." and 2,3-dimethylbutadiene synthesized by us previously [4]. Kinetic studies were performed in temperature-controlled vacuum-sealed glass ampoules accordingly to the procedure described in Ref. [5], in the temperature range of 403–433 K.

III. Results and Discussion

Kinetic curves of HEMA consumption and HTMC as a target product increase are shown in Figs. 1a, b. Kinetic anamorfozes of AM are shown in Fig. 2. The interaction between HEMA and DMB with the molar ratio of HEMA:DMB = 1.5:1 at initial sites (Figs. 1a, 2) completely describe the kinetic equation for the second order irreversible reactions revealed by the kinetic studies.

For the experimental data we used the method of least squares for the dependence $(1/[C_1]_0-[C_2]_0)\times\ln([C_1]\times[C_2]_0/[C_1]_0\times[C_2]t) = k\times t$ [15] for anamorfoze of the second order with non-equivalent ratio of reactants, because the kinetic study was carried out at the DMB:HEMA ratio equalled to 1.5:1. Reaction rate constants were determined by the of dependence character of the slope of the kinetic curves (Table 1).

One can see from Table 1 that the value of the second order constants increases with the increase in temperature of cycloaddition between DMB and HEMA. It is known that the rate constant dependence on the temperature is described by the Arrhenius equation. It helps to determine the activation energy and other activation parameters of the process. The correlation coefficient is satisfactory ($R^2 \approx 0.96$). The dependence of the reaction rate constant upon the temperature is shown in Fig. 3.
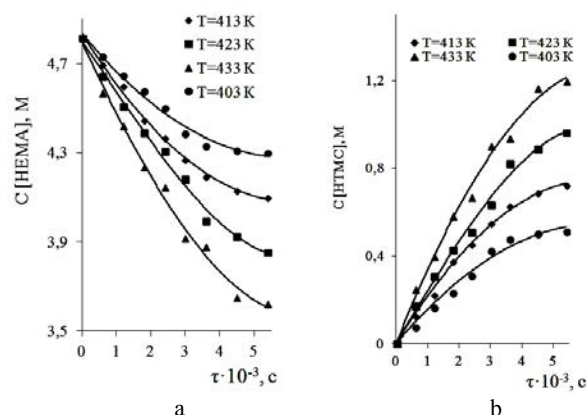

Fig. 1 Kinetic curves of HEMA consumption (a) and HTMC increase (b) at the molar ratio DMB:HEMA= 1.5:1 in the temperature range of 430–433 K

TABLE 1

DEPENDENCE OF RATE CONSTANTS OF CYCLIZATION BETWEEN DMB AND HEMA ON TEMPERATURE AT MOLAR RATIO DMB:HEMA = 1.5:1

Temperature, K	$(k \pm \Delta k)\cdot 10^{-6}$, l/(mol·s)	Δk, %	HEMA, conversion, %
403	2.2±0.1	4.2	11.1
413	4.2±0.2	4.6	17.2
423	6.9±0.3	4.8	24.9
433	10.1±0.4	4.3	28.4

The activation energy is identified from the presented dependence (Fig. 3). The thermodynamics parameters of the activating state – change of enthalpy ΔH and entropy ΔS – are evaluated accordingly to the Eyring equation (Table 2).
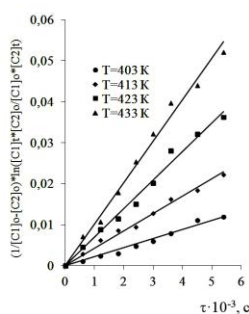
Fig. 2. Anamorfoze of HEMA consumption in the temperature range of 430–433 K at the molar ratio DMB:HEMA= 1.5:1
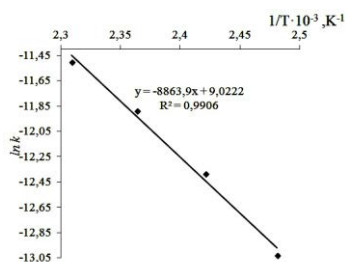

Fig. 3. Dependence of Arrhenius of cycloaddition between DMB and HEMA

TABLE 2

ACTIVATION PARAMETERS
FOR THE CYCLIZATION BETWEEN DMB AND HEMA

$E^{\#} \pm \Delta E^{\#}$, kJ/mol	$\Delta H^{\#}$, kJ/mol	$\Delta S^{\#}$, J/mol·K	lgA	A, l/(mol·s)
73.7±7.2	62	-181	9.02	1.04×10^{10}

The value of activating energy E_{act}= 73.7 kJ/mol shows that under experimental conditions the process is not controlled by the diffusion, but takes place in the kinetic area. A high negative value of activation entropy of the cyclization process (181 J/(mol·K)) and value of enthalpy for the activated state as 62 kJ/mol are typical for Diels-Alder reactions. Bonds opening and formation in these reactions occur synchronously, and energy consumption for one bond opening in the transitional state is compensated by the energy of another bond formation. It means that investigated reaction is energetically favourable.

The investigated reaction is subordinated to the second order of kinetic law, which is confirmed by obtained rate constants and activation parameters of cycloaddition between DMB and HEMA. It is also confirmed by straightening of kinetic curves in anamorfoze of the second order reaction.

To determine the optimal conditions of cycloaddition between DMB and HEMA that provides maximum HTMC yield, the effect of temperature and reactants molar ratio on the yield of target product was studied. To determine the effect of molar ratio the researches were conducted at 433 K and molar ratio of DMB:HEMA = 1: 4; 1: 1.5; 1: 1; 1.25:1; 1.5: 1; 1.75:1 and 2.5:1. The HTMC yield increases from 83 to 87 % with the increase of DMB:HEMA excess from 1:1 to 1.5:1. The further

increase of DMB excess does not cause the essential increase of HTMC yield. In addition, large DMB excess is not profitable from the industrial point of view.

The influence of DMB:HEMA molar ratio on HTMC yield is shown in Fig. 4a. The optimum molar ratio DMB:HEMA was 1.5:1, because the following changes do not essentially increase the product yield. To determine the effect of temperature on cycloaddition between DMB and HEMA the researches were conducted in the temperature range of 393–443 K at the molar ratio of DMB:HEMA = 1.5 : 1. The HTMC yield increases from 83 to 87 % with the increase in temperature from 393 to 433 K. The increase of HTMC yield is not observed with further temperature increase. The effect of temperature on HTMC yield is shown in Fig. 4b.

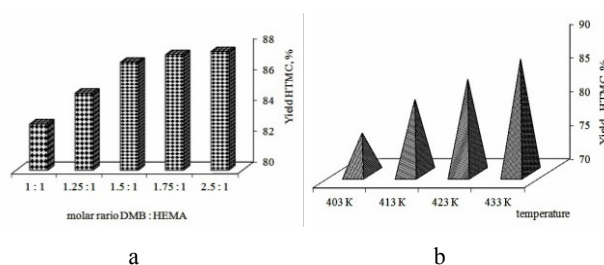a   b

Fig. 4. a) The influence of DMB:HEMA molar ratio
on HTMC yield at 433°K;
b). The effect of temperature on HTMC yield
at the molar ratio DMB:HEMA = 1.5:1.

The optimal temperature range of 423–433°K was selected from Fig. 6, because it provides maximum of HTMC yield. Under chosen conditions HTMC synthesis was provided and physico-chemical characteristics were determined. Synthesized HTMC has the following physicochemical characteristics: $T_{boil.}$= 379 K at 4 gPa; n^{20}_{D}=1.4861; d^{20}_{4} =1.0582; MR found 53.8 ; calc. 53.4.

Conclusion

The kinetics of initial areas of HEMA and DMB interaction has been investigated. On the basis of kinetic regularities the optimal conditions of the process cyclization were determined: temperature of 423–433K and molar ratio of DMB:HEMA = 1.5:1. Such conditions provide a satisfactory rate of cycloaddition between DMB and HEMA and allow to obtain HTMC yield of 84–87 % at the process productivity of 104 g/l·h.

References

[1] NewmanM. *et al*. (Oct. 2, 1992). US Pat. 5175143.
[2] Smets J. *et al*. (Aug. 21, 2008). US Pat. 2008/0200359.
[3] Velazquez J., Hertenstein S., Clare J. *et al*. (Jun. 17, 2010). US Pat. 2010/0152083.
[4] Polyova I., Marshalok G., Fedevych M. *et al*. (June 25, 2011). UA Pat. 60501, MPK C 07 C 13/20.
[5] Polyova I., Polyugyn I., Marshalok G. and Gladij A. (2011). III Ukrainian Science conference of students and phD students " Chemical Karazinsky reading - 2011". Ukraine, Kharkiv 2011, 41.