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KINETICS OF ALLYL-1,3,4-TRIMETHYLCYCLO-HEX-3-ENCARBOXYLATE OBTAINING

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Abstract. Kinetic regularities of allyl-1,3,4-trimethyl-cyclohex-3-encarboxylate obtaining has been investigated. On the basis of the obtained results the optimal conditions of the target product synthesis have been established.
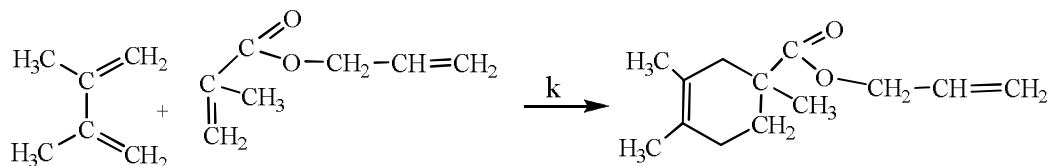
Keywords: 2,3-dimethylbuta-1,3-diene, allylmethacry-late, allyl-1,3,4-trimethylcyclohex-3-encarboxylate.

1. Introduction

Researches in chemistry of alkylcyclohexene compounds are currently occupying an important place alongside other classic chemistries.

Alkylcyclohexene derivatives include a large number of important substances such as antibiotics, drugs that inhibit biosynthesis of cholesterol and significantly reduce its level in blood, anticonvulsant drugs, food flavorings, taste food components, perfume compositions and cosmetics, plant growth activators, modifiers of epoxy resins, plasticizers, and comonomers. Lately alkylcyclohexene compounds have been used as a source for new base polymer materials. Multifunctional monomers with different structure and predetermined set of physical and chemical characteristics [1-7] were synthesized on their basis.

Optically-active liquid crystals are used as a component of liquid crystals composition for electrooptical devices due to their dielectric anisotropy properties. They are synthesized on the basis of alkylcyclohexene derivatives.

Alkylcyclohexene derivatives are also 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.* alkylcyclohexene-carboxylates, 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 [8]. They are valuable raw materials for the perfume compositions, because they have the pleasant floral, citrus and refreshing scents [9]. Optical lenses are received by alkylcyclohexe-necarboxylates polymerisation.

In this work kinetics of allyl-1,3,4-trimethyl-cyclohex-3-encarboxylate obtaining was investigated and optimal conditions for its synthesis using the Diels-Alder reaction were established.

2. Experimental

Allyl-1,3,4-trimethylcyclohex-3-encarboxylate (ATMC) was synthesized by us for the first time [3] using allyl ester of methacrylic acid (AM) and 2,3-dimethylbuta-1,3-diene (DMB). For synthesis we used AM mark "c.p." and DMB synthesized by us previously [4, 5]. The reaction is illustrated as follows:

Kinetic studies were performed in temperature-controlled vacuum-sealed glass ampoules accordingly to the procedure described in Ref. [6], in the temperature range of 403–433 K. AM and DMB with the molar ratio of 1:1.5 were loaded in the ampoules of 10 cm^3, and then hydroquinone was added (1 mas %). The ampoules were

sealed and placed in a thermostat. After definite interval the ampoules were taken out from the thermostat, quickly cooled and opened. The reaction mixture was analyzed by a gas-liquid chromatography device SELMI CHROM-1, using computer registration. Quantitative analysis was performed using internal normalization method. Error of chromatographic analysis for several parallel measurements did not exceed 3 %.

3. Results and Discussion

Kinetic curves of AM consumption and ATMC as a target product increase are shown in Figs. 1a, b. Kinetic anamorfozes of AM are shown in Fig. 2. The interaction between AM and DMB with the molar ratio of AM: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. Also these results are in agreement with literature data for

similar purposes, in particular with the interaction between diethylazodicarboxylate and unsaturated fatty acids [14]. For the experimental data we used the method of least squares for the dependence $(1/[C_1]_0 - [C_2]_0) \cdot \ln([C_1] \cdot [C_2]_0/[C_1]_0 \cdot [C_2]_t) = k \cdot t$ [15] for anamorfoze of the second order with non-equivalent ratio of reactants, because the kinetic study was carried out at the DMB:AM 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 AM. 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.
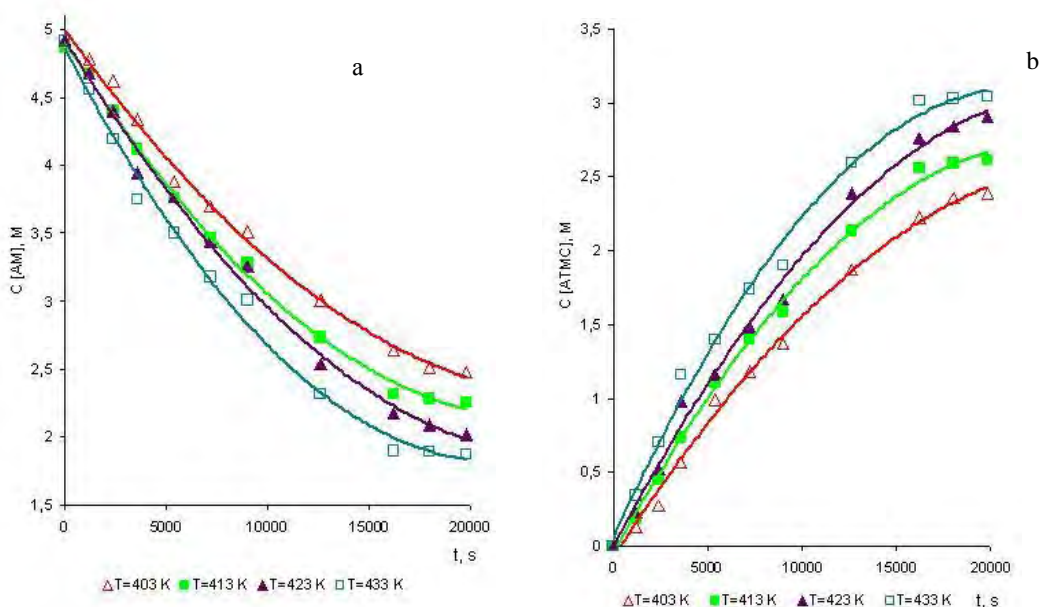

Fig. 1. Kinetic curves of AM consumption (a) and ATMC increase (b) at the molar ratio DMB:AM = 1.5:1 in the temperature range of 430–433 K

Table 1

Dependence of rate constants of cyclization between DMB and AM on temperature at molar ratio DMB:AM = 1.5:1

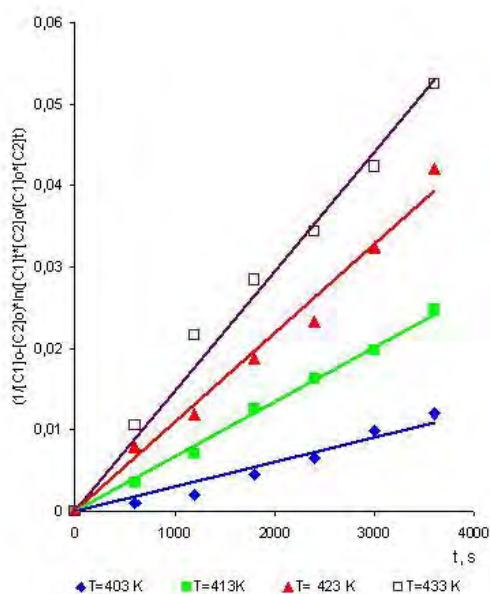| Temperature, K	$(k \pm \Delta k) \cdot 10^{-5}$, l/(mol·s)	AM conversion, %
403	3.0±0.1	24
413	6.7±0.2	27
423	10.9±0.3	31
433	14.7±0.5	33

Fig. 2. Anamorfoze of AM consumption in the temperature range of 430–433 K at the molar ratio DMB:AM = 1.5:1
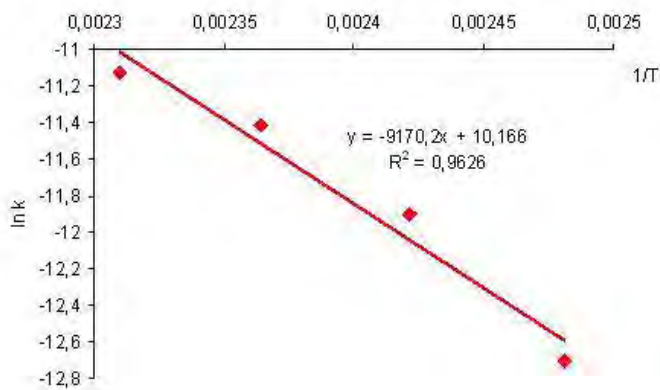

Fig. 3. Temperature dependence of rate constants for cycloaddition between DMB and AM

Table 2

Activation parameters for the cyclization between DMB and AM

$E \pm \Delta E$, kJ/mol	ΔH, kJ/mol	ΔS, J/mol·K	lg$A$,	A, l/(mol·s)
76.2±9.57	79.6	-172	10.2	$2.6 \cdot 10^{10}$

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 [15] (Table 2).

The value of activating energy E_{act}= 76.2 kJ/mol shows that under experimental conditions the process is not controlled by the diffusion, but takes place in the kinetic area [16]. A high negative value of activation entropy of the cyclization process (172 J/(mol·K)) and value of enthalpy for the activated state as 79.6 kJ/mol are typical for Diels-Alder reactions [17]. 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 [18]. 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 AM. 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 AM that provides maximum ATMC 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:AM = 1: 4; 1: 1.5; 1: 1; 1.25:1; 1.5: 1; 1.75:1 and 2.5:1. The ATMC yield increases from 89 to 97 % with the increase of DMB:AM excess from 1:1 to 1.5:1. The further increase of DMB excess does not cause the essential increase of ATMC yield. In addition, large DMB excess is not profitable from the industrial point of view. The influence of DMB:AM molar ratio on ATMC yield is shown in Fig. 4.

The optimum molar ratio DMB:AM 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 AM the researches were conducted in the temperature range of 393–443 K at the molar ratio of DMB:AM = 1.5:1. The ATMC yield increases from 83 to 97 % with the increase in temperature from 393 to 433 K. The increase of ATMC yield is not observed with further temperature increase. The effect of temperature on ATMC yield is shown in Fig. 5.
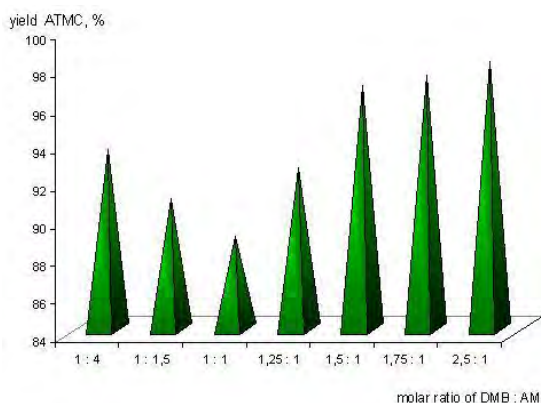
Fig. 4. The influence of DMB:AM molar ratio on ATMC yield at 433°K; process duration is 10 h

Fig. 5. The effect of temperature on ATMC yield at the molar ratio DMB:AM = 1.5:1; process duration is 10 h

The optimal temperature range of 423–433°K was selected from Fig. 5, because it provides maximum of ATMC yield. Under chosen conditions ATMC synthesis was provided and physico-chemical characteristics were determined.

Synthesized ATMC has the following physico-chemical characteristics: $T_{boil.}$= 375 K at 3 mm Hg; n^{20}_D 1.4758; d^{20}_4 0.9565; MR found 61.31; calc. 61.09. ^{1}H NMR spectrum was registered by the spectrometer Bruker AM-300 (300 MHz) in CDCl$_3$ using TMS as the internal standard. ^{1}HNMR spectrum is in agreement with ATMC structure. The spectrum has signals at 1.38, 1.82, 1.82, 1.84, 1.91, 1.2, 2.09, 2.15, 2.40, 4.75, 5.23, 5.24 and 6.6 ppm. Allyl fragment protons are recorded at 6.6 ppm as a multiplet; at 5.23 and 5.24 ppm as a triplet and at 4.75 ppm as a doublet. Six protons of cyclohexene fragment give four doublet signals at 1.84, 1.91, 1.2, 2.09, 2.15 and 2.40 ppm. Methyl groups of a cycle in 1,3,4 position resonate as two singlets at 1.38, 1.82 and 1.82 ppm.

4. Conclusions

The kinetics of initial areas of AM and DMB interaction has been investigated. On the basis of kinetic regularities the optimal conditions of the process cyclization were determined: temperature of 423–433 K and molar ratio of DMB:AM = 1.5:1. Such conditions provide a satisfactory rate of cycloaddition between DMB and AM and allow to obtain ATMC yield of 93–97 % for 10 h at the process productivity of 110 g/l·h. The structure of the obtained product is determined and confirmed by the refractometric analysis and ^{1}H NMR spectroscopy.

References

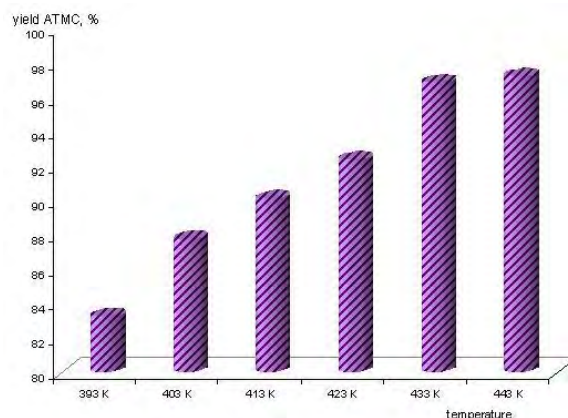[1] Meek J. and Ragsdale J.: J. Am. Chem. Soc., 1948, **70**, 2502.
[2] Petrov A. and Sopov N.: Zh. Obshchei Khimii, 1948, **18**, 1781.
[3] Monnin J. and Neuchatel K.: Angewandte Chemie, 1957, **69**, 762.
[4] Schenk H. and Hanspeter P.: US Pat. 4570648, Publ. Feb. 18, 1986.
[5] Newman M. *et al.*: US Pat. 5175143, Publ. Oct. 2, 1992.
[6] Kunz F. and Polansky O.: Monatshefte fur Chemie, 1969, **100**, 920.
[7] Schenk H. and Hanspeter P.: US Pat. 4113663, Publ. Apr. 10, 1977.
[8] Smets J. *et al.*: US Pat. 2008/0200359, Publ. Aug. 21, 2008.
[9] Velazquez J., Hertenstein S., Clare J. *et al.*: US Pat. 2010/0152083, Publ. Jun. 17, 2010.
[10] Polyova I., Marshalok G., Fedevych M. *et al.*: UA Pat. 60501, MPK C 07 C 13/20. Publ. June 25, 2011.
[11] Polyova I., Marshalok G., Fedevych M. *et al.*: UA Pat. 46772, MPK C 07 C 11/00. Publ. Jan. 11, 2010.
[12] Polyova I., Marshalok G., Fedevych M. *et al.*: UA Patent 52884, MPK C 07 C 11/00. Publ. Sept. 10, 2010.
[13] Polyova I., Polyugyn I., Marshalok G. and Gladij A.: III Vseukrainska Naukova Konf. Studentiv ta Aspirantiv "Himichni Karazinski chytannya -2011". Ukraine, Kharkiv 2011, 41.
[14] Gast L., Bell E. and Teeter H.: J. Am. Oil Chem. Soc., 1956, **33**, 278.
[15] Shmidt R. and Sapunov V.: Neformalnaya Kinetika. V Poiskach Putej Khimicheskikh Reakcij. Mir, Moskwa 1985.
[16] Vasserman A.: Reakciya Dilsa- Aldera. Mir, Moskwa 1968.
[17] Pataya S. (Ed.): Khimiya Alkenov. Khimiya, Leningrad 1969.
[18] Ingold K.: Teoreticheskie Osnovy Organicheskoj Khimii. Mir, Moskwa 1973.

КІНЕТИКА ПРОЦЕСУ ОДЕРЖАННЯ АЛІЛ-1,3,4-ТРИМЕТИЛЦИКЛО-ГЕКС-3-ЕНКАРБОКСИЛАТУ

Анотація. Досліджено кінетичні закономірності процесу одержання аліл- 1,3,4-триметилциклогекс-3-енкарбоксилату. На основі отриманих результатів встановлено оптимальні умови синтезу цільового продукту.

Ключові слова: 2,3-диметилбута-1,3-дієн, алілметакрилат, аліл-1,3,4-триметилциклогекс-3-енкарбоксилат.