Effect of the Reactants Molar Ratio on the Kinetics of Cycloaddition of 2,3-Dimethylbuta-1,3-diene to Allyl Methacrylate

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Abstract—The cycloaddition reaction between 2,3-dimethylbuta-1,3-diene and allyl methacrylate proceeds by the second order kinetics. The rate constants increase with the increase in the excess of one of the reactants. The change in the effective rate constants is described by the Michaelis–Menten equation indicating that the reaction proceeds through the initial equilibrium stage of formation of an intermediate complex which then transforms into the product. The effective rate constants, the equilibrium constants of formation of the intermediate complex, and the rate constant of its transformation into the reaction product were determined, as well as the thermodynamic parameters of the formation of the intermediate complex and the activation parameters of the transformation of the intermediate complex into the product. The limiting stage of the reaction is established and its mechanism is suggested.

Alkylcyclohexene carboxylates are starting materials for drugs, as well as modifiers, plasticizers, epoxy resins, and co-monomers [1]. They are used to create lotions, body emulsions, shampoos, day and night creams, perfumes, and food flavors [2].

In this work we studied the kinetics of interaction between 2,3-dimethylbuta-1,3-diene and allyl methacrylate to optimize the process of producing allyl 1,3,4-trimethylcyclohex-3-ene-1-carboxylate (**I**).

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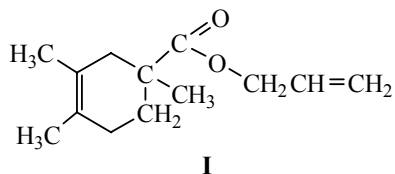
Kinetic studies were performed in temperature-controlled sealed glass ampules according to the method described in [3], in the temperature range 130–160°C. To the 10 cm^3 ampules were charged allyl methacrylate and 2,3-dimethylbuta-1,3-diene in the molar ratios from 1:1 to 1:1.75 and some hydroquinone, the ampules were sealed and placed in a thermostat. At regular intervals, an ampule was re-

moved from the thermostat, quickly cooled, opened, and the reaction mixture was analyzed by gas–liquid chromatography on a SELMI CHROM-1 apparatus. The quantitative analysis was performed with internal normalization. The accuracy of chromatographic analysis in multiple parallel determinations did not exceed 3% [4].

The investigated reaction proceeds according to the second-order kinetics. The values of effective rate constants are listed in Table 1.

We found that the values of the effective second-order constants increase with the increasing ratio 2,3-dimethylbuta-1,3-diene:allyl methacrylate. The difference is more pronounced at higher temperatures. It was appropriate to examine in more detail the mechanism of this reaction. Note that the mechanism of the [4+2] cycloaddition reaction today is still controversial [5]. Two concerted mechanism are suggested: a single-step (sinchronous) and a two-step, in which the first step is the limiting one [6].

The Arrhenius equation described satisfactorily the dependence of the effective rate constants on temperature for different ratios (Fig. 1), which allowed

Table 1. Effective rate constants and activation parameters of the cycloaddition reaction between 2,3-dimethylbuta-1,3-diene and allyl methacrylate

Allyl methacrylate:2,3-dimethylbuta-1,3-diene (mol)	$(k_{ef} \pm \Delta k) \times 10^6$, l mol^{-1} s^{-1}				E_{ef}, kJ mol^{-1}	ΔH_{ef}, kJ mol^{-1}	ΔS_{ef}, J mol^{-1} K^{-1}
	130°C	140°C	150°C	160°C			
1:1	2.0±0.1	3.6±0.1	5.6±0.2	8.9±0.3	71.4	74.4	−188
1:1.25	2.4±0.1	4.6±0.1	7.3±0.2	10.6±0.3	71.5	74.9	−185
1:1.4	2.7±0.1	5.8±0.2	8.9±0.3	12.5±0.4	73.2	76.6	−180
1:1.5	3.0±0.1	6.7±0.2	10.9±0.3	14.7±0.5	76.2	79.6	−171
1:1.6	3.4±0.1	7.9±0.2	12.6±0.4	17.3±0.5	77.9	81.3	−166
1:1.75	4.2±0.1	9.9±0.3	16.5±0.5	23.5±0.7	82.7	86.1	−153

us the calculation of the formal activation energy and other activation parameters of the overall process (Table 1). The correlation coefficient was satisfactory in all cases ($R^2 > 0.95$). The analysis of the parameters made it possible to establish that upon increase in the 2,3-dimethylbuta-1,3-diene excess and the accompanying increase in the values of k_{ef} a systematic increase was observed in the effective energy (ΔE_{ef}) and the effective activation enthalpy (ΔH_{ef}). Simultaneously, the value of the effective activation entropy ($-\Delta S_{ef}$) also increased.

For all ratios of reagents an isokinetic relationship was observed with a high degree of correlation ($R^2 =$

0.99) between the effective entropy and enthalpy of reaction, which allowed the calculation of the isokinetic temperature $T_{iso} = 65°C$ (Fig. 2) that was far from the investigated temperature range.

The increase in E_{ef} and ΔH_{ef} with increasing excess of 2,3-dimethylbuta-1,3-diene and a simultaneous increase in ΔS_{ef} indicate the increasing steric hindrances in the reaction course. This finding suggests also that the reaction mechanism is unique in the studied range of the reagents ratio.

Such a systematic change in the rate constants with an increase in excess of one of the reactants is typical of the reactions that include the formation of the charge transfer complex (CTC by the reagents) [7, 8]. A similar reaction course has been proved also for several cases, including the alcoholysis of alcohols [9, 10], where the formation of charge-transfer complexes was confirmed by the methods of physicochemical and spectral analyses.

For these reactions the effective second-order rate constant does not remain constant at the change in the reagent ratio, and the kinetics of the process is described by the Michaelis–Menten equation:
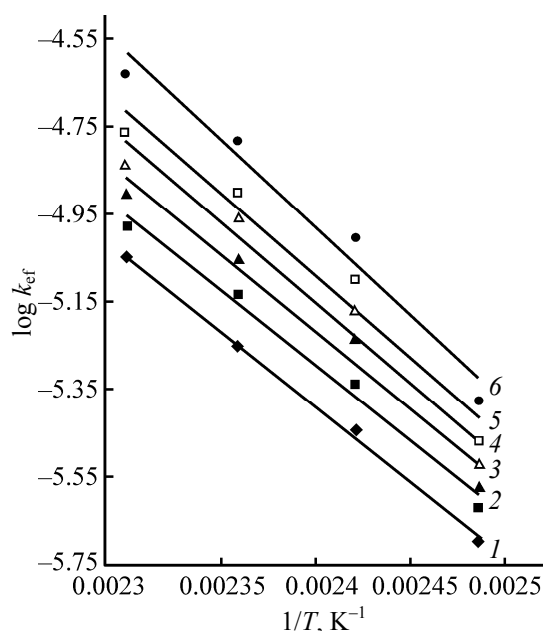

Fig. 1. Dependence of the effective rate constant of cycloaddition between 2,3-dimethylbuta-1,3-diene and allyl methacrylate on temperature for different ratios of reactants: 2,3-dimethylbuta-1,3-diene: allyl methacrylate = (*1*) 1:1, (*2*) 1.25:1, (*3*) 1.4:1, (*4*) 1.5:1, (*5*) 1.6:1, and (*6*) 1.75:1.
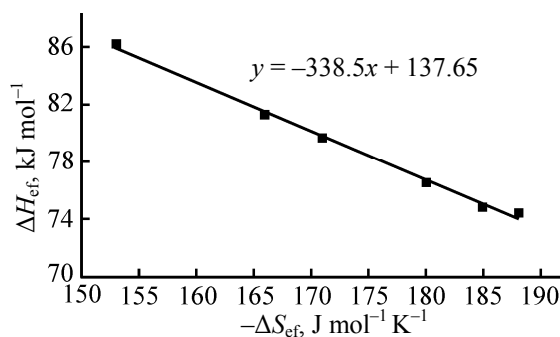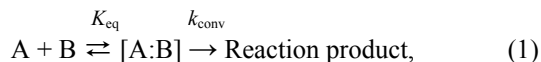

Fig. 2. Dependence of the effective activation entropy on the effective activation enthalpy of the cycloaddition of 2,3-dimethylbuta-1,3-diene to allyl methacrylate.

$$A + B \underset{K_{eq}}{\overset{k_{conv}}{\rightleftarrows}} [A:B] \rightarrow \text{Reaction product,} \quad (1)$$

$$1/k_{ef} = 1/k_{conv} + (K_{eq}c_A)/(k_{conv}), \quad (2)$$

where k_{ef} is experimentally determined effective second order rate constant (l mol^{-1} s^{-1}) for each reagent ratio, K_{eq} is the equilibrium constant (l mol^{-1}) for the intermediate complex formation, k_{conv} is the rate constant (s^{-1}) of the intermediate complex conversion into the reaction product, c_A is the molar concentration (M) of the substance taken in excess.

In our case, the change in the effective rate constants of the 2,3-dimethylbuta-1,3-diene cyclo-addition to allyl methacrylate as a dependence on the ratio of reactants is also satisfactorily described by the Michaelis–Menten equation (2). This fact suggests that the cycloaddition reaction between 2,3-dimethylbuta-1,3-diene and allyl methacrylate proceeds through a stage of equilibrium with the formation of an intermediate complex followed by its conversion into the reaction product [Eq. (3)].
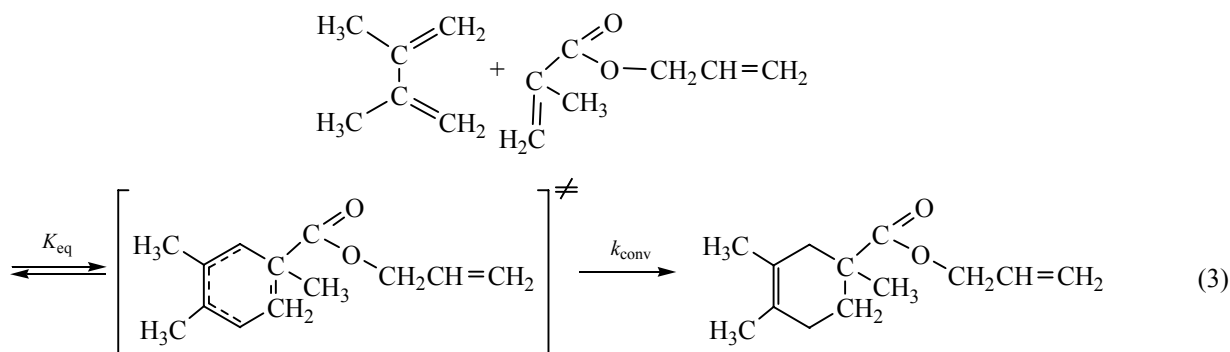
From the dependences shown in Fig. 3 for four temperatures, we obtained the following linear equations:

130°C: $1/k_{ef} = -340146CA + 838510$, ($R^2 = 0.998$), (4)

140°C: $1/k_{ef} = -244294CA + 520041$, ($R^2 = 0.991$), (5)

150°C: $1/k_{ef} = -161490CA + 338760$, ($R^2 = 0.994$), (6)

160°C: $1/k_{ef} = -94241CA + 209279$, ($R^2 = 0.992$). (7)

The slope of the obtained straight lines gives the rate constants of the conversion of the intermediate complex in the reaction product (k_{conv}). The values of the intercepts on the ordinate axis give the equilibrium constants of the complex formation (Table 2) according to the expression $K_{eq} = 1/(k_{ef} k_{conv})$.

The dependence of the equilibrium constant (K_{eq}) of the intermediate complex formation is described by the isobar (Fig. 4, $R^2 = 0.993$). The dependence of the rate constants of conversion (k_{conv}) on temperature is described by the Arrhenius equation (Fig. 5, $R^2 = 0.999$), which allows the calculation of the activation parameters of the intermediate complex conversion in the reaction product (Table 2).

The found positive ΔG_{eq} and negative ΔS_{eq} values indicate the energy advantage of the intermediate complex formation. At the same time a relatively fast decomposition of the intermediate complex suggests that its formation is the limiting stage of the process.

Fig. 3. Dependence of the effective rate constant of cyclo-addition between 2,3-dimethylbuta-1,3-diene and allyl methacrylate on the molar ratio of reagents in the temperature range 130–160ºC.

Thus, we established for the first time that the kinetics of the investigated process obeyed Michaelis–Menten equation, which was valid in the case of the
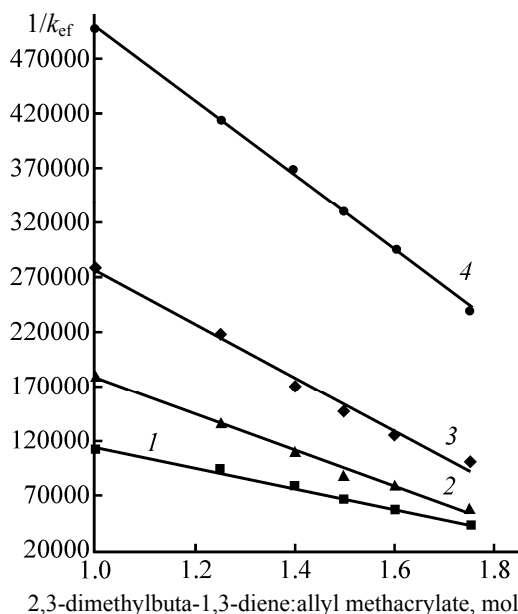
Table 2. Equilibrium constants (K_{eq}) and thermodynamic parameters of formation of the intermediate complex, the rate constants (k_{conv}) and activation parameters of its transformation into a product of the reaction

Constants	130°C	140°C	150°C	160°C	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}	ΔG, kJ mol^{-1}
$K_{eq} \times 10^{11}$, l mol^{-1}	2.85	1.27	0.54	0.19	8.5	−250	96
$k_{conv} \times 10^{6}$, s^{-1}	1.19	1.92	2.95	4.78	70.1	−204	66.7[a]

[a] E_{conv}.

reaction course through the stage of the associative equilibrium . It is an argument in favor of this reaction to proceed by the mechanism of concerted cycloaddition. However, the nature of the interaction of the components should be studied in more detail. It is known that the addition of a diene molecule to the dienophile double bond originates from a certain deficiency of the electron density on this double bond due to its interactions with the other active groups, and the stronger conjugation with them, the easier the diene addition. Indeed, while $k_{ef.}$ of 2,3-dimethylbuta-1,3-diene interaction with allyl methacrylate at 80°C is $0.74 \times \times 10^{-6}$ mol l^{-1} s^{-1} (determined graphically), the k_{ef} for the interaction of 2,3-dimethylbuta-1,3-diene with 1,4-naphthoquinone, where the π-bond interacts with two C=O groups, is 0.14×10^{-5} mol l^{-1} s^{-1} (in hexane) [11], and with its 5-substituted derivatives it is even two orders of magnitude higher, 1.5×10^{-3} mol l^{-1} s^{-1} [12]. The accelerating effect of electronegative substituents, like cyano group or halogen, on the cycloaddition reaction is even more pronounced. Thus, in the interaction of cyclopentadiene with methyl acrylate at 30°C in dioxane k_{ef} is 2.8×10^{-5} mol l^{-1} s^{-1}, with fumaric acid dinitrile, 155×10^{-5} mol l^{-1} s^{-1}, and with tetracyanoethylene, 10200×10^{-5} mol l^{-1} s^{-1}. In such cases it is reasonable to assume that a relatively strong donor–acceptor bond arises between the reagents [13].

The results of the study of kinetic regularities in the process of synthesis of allyl 1,3,4-trimethylcyclohexa-3-ene-1-carboxylate and the study of the mechanism of this reaction showing its corresondence to the Michaelis–Menten equation confirm the formation of an intermediate complex between the reagents, 2,3-dimethylbuta-1,3-diene and allyl methacrylate. The study of thermodynamic parameters of formation of the intermediate complex suggests that the limiting stage is the slow formation of an intermediate complex, the activation parameters of the transformation of the intermediate complex in the product indicate that the conversion of the intermediate complex in the product occurs rapidly and spontaneously.
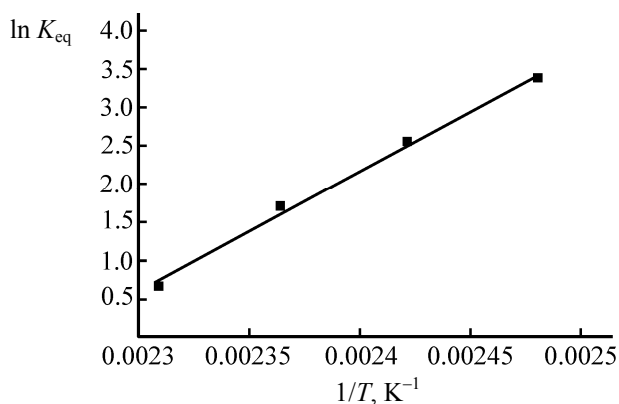
Fig. 4. Dependence of the equilibrium constant of the formation of intermediate complex on the temperature.
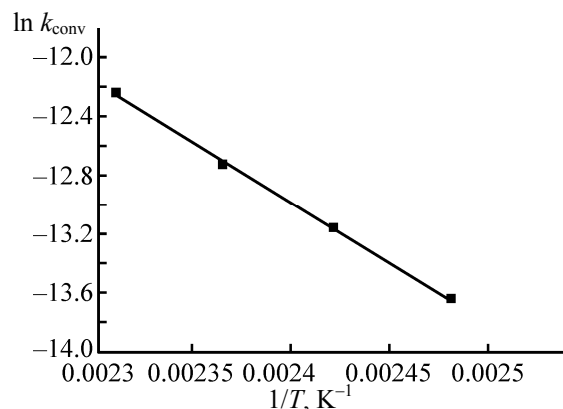
Fig. 5. Dependence of the rate constants of conversion of the intermediate complex in the reaction product on the temperature.

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