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CATIONIC TELOMERIZATION OF 2-METHYL-1,3-BUTADIENE WITH ISOPROPOXYMETHYL CHLORIDE. A MODEL OF KINETICS

Numerous works have been published on the reactions of electrophilic addition of alkoxymethyl chlorides to alkenes and conjugate alkadienes in the presence of aprotic acids [1,2]. However, so far little attention has been paid to a quantitative investigation of these reactions. With a view of filling in this gap, a study of the reaction of 2-methyl-1,3-butadiene (I) with isopropoxymethyl chloride (II) in the presence of zinc chloride has been undertaken by the present authors. Earlier we have established that this reaction produces a monoadduct in approximately 85% of the yield, comprising 88—90% of *E* and *Z* of 1,4-adducts and 10—12% of 1,2-adduct with diene. The composition of polyadducts formed in about 15% of the yield has not been studied thoroughly [3].

To construct a quantitative reaction model [4] we have investigated changes in the material balance of the initial components and the monoadduct formed, as well as the kinetics of the change in the initial chloroether (II) depending on the ratio of the initial reagents and the reaction temperature. The kinetic curves are presented in Fig. 1.

To elucidate the chemism of the reaction and to construct its conversion model [4], changes in the component concentrations were plotted on the dimensionless graph depicted in Fig. 2. As can be seen, the highest yield of monoadducts is obtained at the ratio of ingredients of (I):(II) = 1.2:1. By excess (I) higher adducts are formed more abundantly.

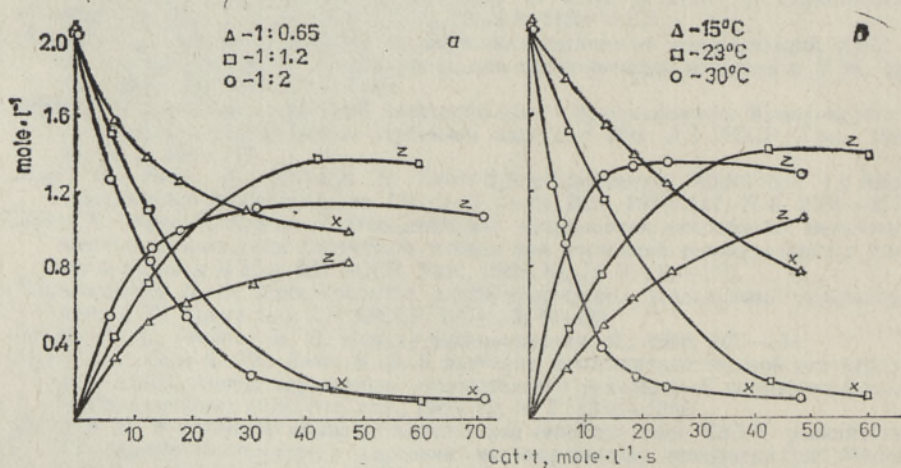


Fig. 1. Changes in the concentration of the initial telogen (*x*) and the monoadduct formed (*z*) depending on reaction time: a — the effect of the telogen:taxogen ratio at 23°C, b — the effect of the reaction temperature at the telogen:taxogen ratio 1:1.2.

However, excess (II) does not decrease the formation of polyadducts significantly. A change in the quantity of diene (I) reacted at an ingredient ratio of (I):(II)=1.2:1 is especially remarkable. Thus, in the beginning of the reaction the formation of higher adducts with a high taxogen content (I) is observed, in the end of the reaction the telogen (II) content of polyadduct increases, which, however, has no significant influence upon the relative rate of formation of monoadduct from (II). On the basis of the above observations it may be assumed that polyadducts in the given reaction result from telomerization of diene (I). At the same time, the higher telomers in a consecutive reaction add to the initial chloroether (II) that may account for its high content in polyadducts at high degrees of conversion or by the deficiency of diene.

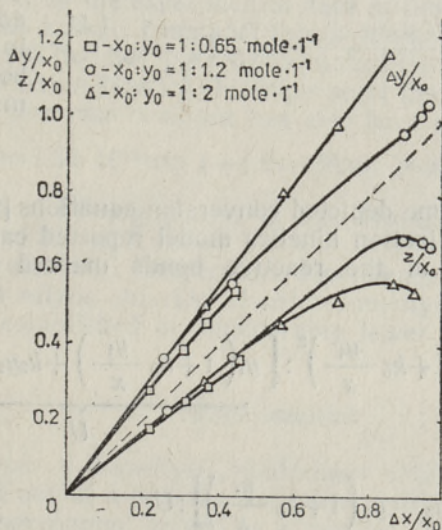
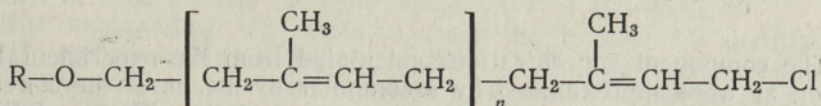
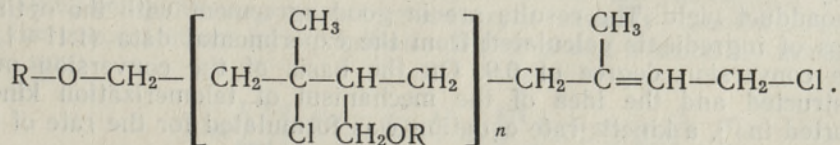


Fig. 2. Integral (graphic) conversion model of the reaction, $\Delta x = x_0 - x$, $\Delta y = y_0 - y$.

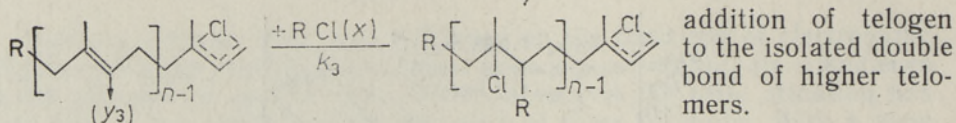
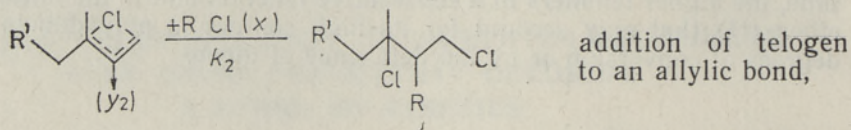
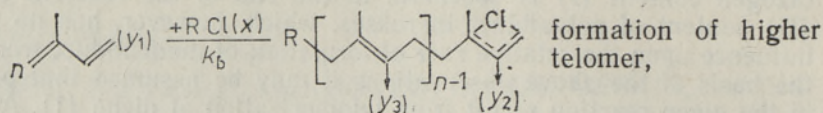
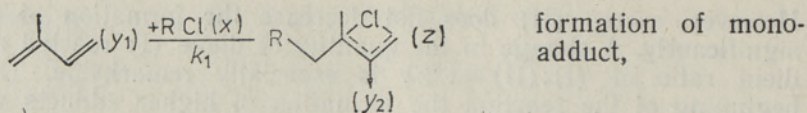
Consideration of a possible chemical structure of the higher telomers formed



allows us to make the conclusion that it is the addition of (II) to the isolated trisubstituted unsaturated bonds of polyadducts that represents such a consecutive reaction with the formation of the following compounds:



Taking into consideration the fact that telomerization of trialkyl-substituted alkenes proceeds to a low extent^[5, 6], the following, somewhat simplified chemical reaction scheme may be suggested for the given system:



For the reaction scheme depicted conversion equations [4] may be set up by applying the telomerization kinetics model reported earlier [7, 8] (designating concentrations of the reactive bonds marked by letters in the Scheme):

$$\frac{dy_1}{dx} = y_1 \left(1 + k_b \frac{y_1}{x} \right)^2 : \underbrace{\left[y_1 \left(1 + k_b \frac{y_1}{x} \right) + k_2 y_2 + k_3 y_3 \right]}_U,$$

$$\frac{dy_2}{dx} = \left[k_2 y_2 - y_1 \left(1 + k_b \frac{y_1}{x} \right) \right] : U,$$

$$\frac{dy_3}{dx} = \left[k_3 y_3 - k_b \frac{y_1^2}{x} \left(1 + k_b \frac{y_1}{x} \right) \right] : U,$$

$$\frac{dz}{dx} = [k_2 z - y_1] : U.$$

The component concentrations calculated from the experimental data (x , y_1 , z) were approximated by a computer by means of the conversion model constructed, using the least squares technique [9]. The following values of the constants searched for were obtained: $k_b=0.18$; $k_2=0.02^*$; $k_3=1.43$, whereas the average deviation of the calculated data from experimental ones $\sigma = \pm 0.06$. Then, by means of the conversion model set up, the ratios of ingredients were searched for to obtain an optimum monoadduct yield. The results are in good agreement with the optimum ratios of ingredients calculated from the experimental data (I:II=1.2:1) at a conversion degree of 0.9. On the basis of the conversion model constructed and the idea of the mechanism of telomerization kinetics reported in [7], a kinetic rate equation was formulated for the rate of telogen concentration, (x):

* Taken from the value of k_2/k_3 calculated earlier for telomerization of y_2 and y_3 with allyl chlorides [10].

$$\frac{dx}{dt} = \frac{[\text{cat.}] \cdot k \cdot x \left(y_1 + k_b \frac{y_1}{x} + k_2 y_2 + k_3 y_3 \right)}{1 + \frac{\bar{r}_s s}{x} + \bar{r}_y \left(y_1 + k_b \frac{y_1^2}{x} + k_2 y_2 + k_3 y_3 \right) + \frac{\bar{r}_p y_1^2}{x}}$$

where [cat] — catalyst concentration, x , y_1 — ingredients concentrations; s — concentration of active ligands of the catalyst in the reaction medium; equilibrium constants: \bar{r}_s — of the formation of a complex of the catalyst with oxygen-containing admixtures of the medium, \bar{r}_y — of the formation of activated intermediates of taxogens, \bar{r}_p — of the formation of polytaxogenic intermediates of the reaction, k — total rate.

By approximating the experimental data in time (Fig. 1), the following total and partial kinetic constant values have been determined: $\bar{r}_y = 0$, $\bar{r}_s = 0.01$, $\bar{r}_p = 0.233$ [l·mole⁻¹], $k = 0.045$ [mole⁻²·l²·s⁻¹]. From the data on the dependence of reaction kinetics on temperature the temperature dependence of the total reaction rate constant has also been established:

$$k = 7.53 \cdot 10^{13} \exp(-1.04 \cdot 10^4/T), \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{s}^{-1}.$$

This shows that a 10°-degree rise in temperature increases the reaction rate by a factor of 3.2—3.4.

Unlike the calculated temperature-dependence constant, for the reaction of (I) with allylic chloride (1-chlor-3-methyl-2-butene) the temperature coefficient established is considerably lower (1.4 [1]).

Experimental

1. The reaction of 2-methyl-1,3-butadiene with isopropoxymethyl chloride was carried out in *n*-pentane according to [3]. A 25% ZnCl₂ solution in nonaqueous isopropanol served as a catalyst. The samples to be analyzed were collected at certain time intervals. The concentration of unreacted isopropoxymethyl chloride (x) was determined according to the procedure described in section 2 in Experimental.

The consumption of initial alkene (I) was calculated by the telomer mass and its chlorine content. The telomer content of the sample was calculated by weighing after the distillation of the initial reagents and the solvent at 2700 Pa and the cube temperature of 40—80°C.

The monoadduct was isolated from the telomer by distillation at 400 Pa and the boiling temperature of 68—70°C. The isomeric composition of the monoadduct was established on a "Chrom-5" chromatograph (Laboratorni Přístroje, Prague, Czechoslovakia) with a flame-ionization detector. Conditions: glass column 24000×0.27 mm, liquid phase tricyanoethoxypropane (TCEP), carrier gas (argon) flow rate 1.5 cm³/min, evaporator temperature 180°C, column temperature 60°C.

The values of the relative kinetic constant were calculated with an EC 1052 computer, approximating the experimentally established changes in the concentrations of the initial substances and adducts by minimizing the sum:

$$F = \sum_i \left(\frac{y_{1i} - \bar{y}_{1i}}{y_{1.0} - y_1} \right)^2 + \sum_i \left(\frac{z_i - \bar{z}_i}{z_i} \right)^2,$$

where y_{1i} , z_i — experimental data, \bar{y}_{1i} , \bar{z}_i — calculated data, $y_{1.0}$ — the initial concentration.

The Rosenbrock method was used to find the minimum.

2. The procedure of determining ROCH_2Cl in the reaction medium. Twenty ml of distilled water is poured into a 100 ml conical flask with a well-lubricated ground stopper, weighed on assay balances and cooled in a refrigerator for 15 min. The sample under analysis containing 2—10 mmoles of isopropoxymethyl chloride is injected into the flask with a glass pipette and a medicinal syringe. The flask is kept at room temperature for 20 min and weighed; 20 ml of hexane is added and then the flask's contents are mixed with a magnetic stirrer. Hexane and water are separated in a separating funnel after a 3-min settling; 10 ml of the sample is extracted from the water layer and diluted with water to 100 ml in a volumetric flask. From the volumetric flask 10 ml of the solution is extracted by means of a pipette, brought into a 200-ml conical flask, 5 drops of the phenolphthalein solution are added and neutralized with 0.1 *n* sodium hydroxide solution. 0.13 *n* dimedone solution is poured from the burette in a quantity ensuring about 20—30% reagent excess (dimedone is dissolved in 2-propanol, diluted with water at a ratio of 1:1). The flask walls are rinsed with 20 ml of 2-propanol and the flask is heated at 90—95°C for 20 min under a reflux condenser. The condenser and the flask walls are rerinsed with 20 ml of 2-propanol, and the flask contents are shaken. The solution should not have any precipitate. After 10-min cooling in ice water 10 drops of phenolphthalein are added into the flask and the contents are titrated with 0.1 *n* sodium hydroxide solution. The content of isopropoxymethyl chloride in the sample under analysis is calculated according to the following formula:

$$\frac{1.006 \cdot 20 (V_1 n_1 - V_2 n_2)}{G} \left[\frac{\text{mmole}}{\text{g}} \right],$$

where *G* — the weight of the sample, g; *V*₁ — the volume of the dimedone solution, ml; *V*₂ — the volume of the sodium hydroxide solution, ml; *n*₁ — normality of the dimedone solution; *n*₂ — normality of the sodium hydroxide solution; 1.006 — the coefficient for calculating the quantity of formaldehyde passing into hexane.

Summary. The chemism of electrophilic addition of isopropoxymethyl chloride to 2-methyl-1,3-butadiene has been elucidated, its conversion and kinetic models have been constructed, and optimum conditions of mono-adducts synthesis have been established. It has been ascertained that in the reaction studied the formation of polyadducts proceeds according to the telomerization mechanism. The isolated trisubstituted alkene bonds of the higher telomers formed are subjected to the reaction with the initial alkoxy methyl chloride. A comparison of the relative constant values of telomerization of 2-methyl-1,3-butadiene with 1-chlor-3-methyl-2-butene (~ 0.2)^[10] obtained in this work (0.18), as well as the relative reactivities by formation of monoadducts of the latter and isopropoxymethyl chloride (1:78)^[12] shows that the chemical nature of telogen plays an important role in the formation of higher telomers. The reactivity of telogen does not exert such remarkable influence on this process. This conclusion, however, requires further specification by investigating telomerization ingredients of various chemical structures.

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2-METÜÜL-1,3-BUTADIËENI JA ISOPROPOKSÜMETÜÜLKLORIIDI KATIOONNE TELOMERISATSIOON. KINEETIKA MUDEL

On uuritud isopropoksümetüülkloriidi elektrofiilset ühinemist 2-metüül-1,3-butadiëeniga, välja selgitatud reaktsiooni kemism ning koostatud konversiooni ja kineetika mudel. On arvatud usaldusväärsed kiiruskonstantide väärtused ja üldise kiiruskonstandi sõltuvus temperatuurist, leitud optimaalsed tingimused monoadukti maksimaalse saagise saamiseks ning kindlaks tehtud, et uuritud reaktsioonis toimub polüadukti moodustumine telomerisatsiooni mehhanismil (ahela kasvu koefitsient 0,18). Sealjuures moodustuvate kõrgemate telomeeride isoleeritud kolmikasendatud alkeensed sidemed astuvad järgnevasse reaktsiooni lähte-alkoksümetüülkloriidiga.

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КАТИОННАЯ ТЕЛОМЕРИЗАЦИЯ 2-МЕТИЛ-1,3-БУТАДИЕНА С ИЗОПРОПОКСИМЕТИЛХЛОРИДОМ. МОДЕЛЬ КИНЕТИКИ

Выявлен химизм, составлены конверсионная и кинетическая модели электрофильного присоединения изопропоксиметилхлорида к 2-метил-1,3-бутадиену. Найдены достоверные значения кинетических констант и определена температурная зависимость для общей константы скорости. Выявлены оптимальные условия для получения максимальных выходов моноаддуктов аллильного строения. Установлено, что образование полиаддуктов в изученной реакции протекает по механизму теломеризации (коэффициент роста цепи 0,18). При этом изолированные трехзамещенные алкеновые связи образующихся высших теломеров вступают в последовательную реакцию с исходным алкоксиметилхлоридом.