

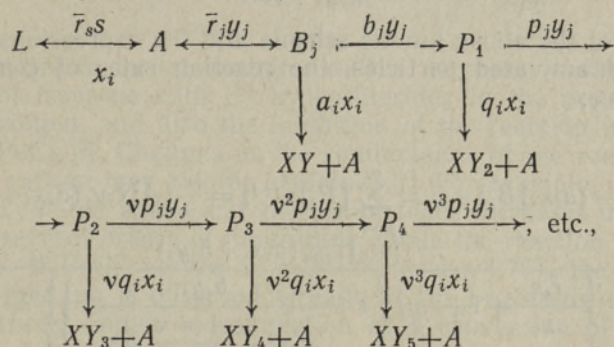
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ON A MODEL OF CATIONIC TELOMERIZATION KINETICS

In a previous communication [1], a reaction mechanism of the cationic telomerization of alkenes is proposed. This involves the initial formation of polarized nonionic monotaxogenic activated complexes (B_j) and polytaxogenic activated ionic intermediates — carbocations (P_j). At the same time they differ from each other in relative reactivity towards chain propagation and transfer. In the kinetic equations [1] the average constants of chain propagation and transfer for polytaxogenic intermediates (p_j and q_i) are treated as independent of the molecular mass of a growing particle (P_j). This may lead to inaccuracies in the description of the reaction kinetics for different concentration ratios of the reactants.

In the present work the possibility of formulating kinetic equations of cationic telomerization is considered. The changes in the molecular mass and reactivity of polytaxogenic reaction intermediates are taken into account. An additional constant is introduced into a kinetic scheme of the reaction (using symbols of [1]) in order to achieve this.



where ν — the constant of the decrease in the reactivity of a polytaxogenic particle in case the chain of its molecule is increased by one taxogen unit.

Taking into account the identity of polytaxogenic intermediates and the reactive centres formed, their selectivity towards chain transfer and propagation of telomerization is assumed to be constant ($p_j \nu^j : q_i \nu^i = \text{const}$).

At low catalyst concentrations $[K_0] : [X] \leq 10^{-2}$, the balance of catalyst complexes is:

$$[K_0] = [L] + [A] + [B_j] + \sum_{j=1}^{\infty} [P_j].$$

According to the kinetic scheme, the concentrations of the catalyst complexes are expressed by

$$[L] = \frac{\bar{r}_s S}{x_i} [A], \quad [B_j] = \bar{r}_j y_j [A], \quad [P_1] = [B_j] \frac{b_j y_j}{p_j y_j + q_i x_i},$$

and those of growing polytaxogenic particles by

$$[P_j] = [P_1] \left[\frac{p_j y_j}{\nu (p_j y_j + q_i x_i)} \right]^{j-1}.$$

According to the sum of an infinite decreasing progression

$$\sum_{j=1}^{\infty} [P_j] = \frac{[P_1]}{1 - \frac{p_j y_j}{v(p_j y_j + q_i x_i)}} = [B_j] \frac{b_j y_j}{q_i x_i - \frac{1-v}{v} p_j y_j},$$

if $p_j y_j < v(p_j y_j + q_i x_i)$.

By introducing the derived values into the catalyst balance we obtain:

$$[A] = \frac{[K_0]}{\frac{\bar{r}_s s}{x_i} + 1 + \bar{r}_j y_j \left(1 + \frac{b_j y_j}{q_i x_i - \frac{1-v}{v} p_j y_j} \right)},$$

The reactivity of polytaxogenic intermediates in the telomerization reaction is expressed as follows:

$$[P_j] v^{j-1} = [P_1] \left[\frac{v p_j y_j}{v(p_j y_j + q_i x_i)} \right]^{j-1};$$

their general reactivity is given by:

$$\sum_{j=1}^{\infty} [P_j] v^{j-1} = \frac{[P_1]}{1 - \frac{p_j y_j}{v(p_j y_j + q_i x_i)}} = [B_j] \frac{b_j y_j}{q_i x_i}.$$

On the basis of the above kinetic scheme and the expressions for the concentrations of activated particles, the reaction rates of components are represented for:

telogen

$$\begin{aligned} \frac{dx_i}{dt} &= -\{a_i x_i [B_j] + q_i x_i \sum_{j=1}^{\infty} [P_j] v^{j-1}\} = -[A] \bar{r}_j y_j (a_i x_i + b_j y_j) = \\ &= -\frac{[K_0] \bar{r}_j y_j (a_i x_i + b_j y_j)}{\left\{ \frac{\bar{r}_s s}{x_i} + 1 + \bar{r}_j y_j \left(1 + \frac{b_j y_j}{q_i x_i - \frac{1-v}{v} p_j y_j} \right) \right\}} = U, \end{aligned}$$

taxogen

$$\begin{aligned} \frac{dy_j}{dt} &= -\{[B_j] (a_i x_i + 2b_j y_j) + p_j y_j \sum_{j=1}^{\infty} [P_j] v^{j-1}\} = \\ &= -[A] \bar{r}_j y_j \left(a_i x_i + 2b_j y_j + b_j y_j \frac{p_j y_j}{q_i x_i} \right) = \\ &= -[K_0] \bar{r}_j y_j \left[a_i x_i + b_j y_j \left(2 + \frac{p_j y_j}{q_i x_i} \right) \right] : U, \end{aligned}$$

the monoadduct

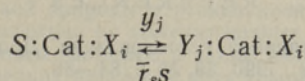
$$\frac{dz_{ij}}{dt} = [B_j] a_i x_i = [A] \bar{r}_j y_j a_i x_i = [K_0] \bar{r}_j y_j a_i x_i : U.$$

As seen, the conversion equations of the reaction $\left(\frac{dz}{dx} [2] \right)$ do not involve the constant v and are identical with those presented in [1]. The constant v is only contained in the general kinetic equation.

It describes a decrease in the reaction rate resulting from the formation of growing polytaxogenic intermediates of lower reactivity. From the kinetic equation presented, it appears that the telomerization process is completely inhibited if

$$\frac{1-v}{v} \frac{p_j y_j}{q_i x_i} \geq 1.$$

By deactivating the monotaxogenic complex (B_j) with nucleophilic ligands (S) of the reaction medium according to a one-step mechanism:



the catalyst balance is:

$$[K_0] = [L] + [B_j] + \sum_{j=1}^{\infty} [P_j].$$

The kinetic equation of telogen will assume a simpler form:

$$\frac{dx_i}{dt} = \frac{[K_0] (a_i x_i + b_j y_j)}{\frac{\bar{\tau}_{sS}}{y_j} + 1 + \frac{b_j y_j}{q_i x_i - \frac{1-v}{v} p_j y_j}}$$

The new kinetic model explains well a decrease in the rate of telomerization of isoprene with its hydrochlorides in the presence of $SnCl_4$ by excess taxogen, and also the inhibition of the reaction in the presence of catalyst $FeCl_3$ [3]. Changes in the conductance of the reaction medium, as observed earlier, may also be explained [4]. For example, in the presence of $SnCl_4$ (calculated $b_j/a_i=0.2$) the conductance increases in the course of reaction by several orders of magnitude, while the reaction rate decreases considerably. If $FeCl_3$ serves as catalyst ($b_j/a_i=1.75$), the high conductance of the medium is observed already at the beginning of the reaction when the process comes to completion at a conversion of 0.15–0.2 [3, 4].

On the basis of the dual mechanism of cationic telomerization presented, also the effect of electrophilicity of the catalysts used on the composition of the reaction products of isoprene and allyl and alkoxymethylchlorides has been interpreted [5, 6]. Thus, in the presence of strong electrophiles ($AlCl_3$, $FeCl_3$), the detachment of a chloride ion from telogen takes place more easily, leading to an intermediate carbocation. The low selectivity of the latter towards chain transfer results in higher telomers. By using milder electrophiles ($SnCl_4$, $ZnCl_2$, $BiCl_3$), the reactions proceed mainly through nonionic coordination complexes with the formation of monoadducts. The relative electrophilicities of the catalysts, as established for the above reactions [5, 6], are not always observed for the lower reactivity systems of telomerization. For example, in the reactions of 1,3-butadiene with tertiary butyl chloride [7], higher telomers are formed mainly in the presence of $SnCl_4$ and $AlCl_3$, while $ZnCl_2$ and $BiCl_3$ favour the formation of monoadducts. This indicates that the formation of carbocations depends, besides the electrophilicity of catalyst and polarizability of the C-Cl bond of telogen, also on the ionization power of the ternary coordination complex of the latter with taxogen. In the kinetics model presented, this is taken into account by the rate constant (b_j) of the formation of a polytaxogenic particle (P_j) from the equilibrium monotaxogenic reaction complex (B_j).

To sum up, kinetic equations of cationic telomerization have been formulated. The equations take into consideration changes in the chemical nature and reactivity of activated intermediates in the transition from monotaxogenic to polytaxogenic particles, as well as the increase in the molecular mass and the decrease in the reactivity of the latter by chain propagation.

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KATIOONSE TELOMERISATSIOONI KINEETIKA MUDELIST

On koostatud katioonse telomerisatsiooni kineetika ja konversiooni võrrandid, mis arvestavad aktiveeritud reaktsiooniintermediaatide keemilise olemuse ja reaktsioonivõime muutumist polariseeritud (mitteioonsete) monotaksogeensete komplekside üleminekul polütaksogeenseteks ioniseeritud kompleksideks, samuti viimaste moolmassi ja reaktsioonivõime muutumist telomerisatsiooniahela kasvades. Reaktsioonikomponentide konversioon lihttelomerisatsioonil on kirjeldatav kineetika võrranditega:

$$\frac{dx_i}{dt} = - \frac{[K_0] \bar{r}_j y_j (a_i x_i + b_j y_j)}{\left\{ \frac{\bar{r}_s s}{x_i} + 1 + \bar{r}_j y_j \left(1 + \frac{b_j y_j}{q_i x_i - \frac{1-v}{v} p_j y_j} \right) \right\}} = U,$$

taksogeenile

$$\frac{dy_j}{dt} = - [K_0] \bar{r}_j y_j \left[a_i x_i + b_j y_j \left(2 + \frac{p_j y_j}{q_i x_i} \right) \right] : U,$$

monoодукtile

$$\frac{dz_{ij}}{dt} = [K_0] \bar{r}_j y_j a_i x_i : U,$$

kus $[K_0]$ on katalüsaatori, x_i telogeeni, y_j taksogeeni, z_{ij} monoодукti ja s keskkonna nukleofiilsete ligandide kontsentratsioon; \bar{r}_j on monotaksogeense aktiveeritud kompleksi tekke ja \bar{r}_s nukleofiilsete ligandidega desaktiveeritud katalüsaatori kompleksi tekke tasakaalukonstant; monotaksogeense reaktsiooniintermediaadi kiiruskonstandid on a_i — telogeeniga,

b_j — taksogeeniga; ditaksogeense reaktsiooni-intermediaadi kiiruskonstandid on q_i — telogeeniga, p_j — taksogeeniga; ν on polütaksogeense intermediaadi reaktsioonivõime langus molekuli ahela kasvades taksogeeni ühiku võrra.

Uus kineetika mudel interpreteerib hästi katalüsaatorite elektrofiilsuse ja ingredientide suhte mõju reaktsiooniproduktide koostisele ning reaktsioonikineetikale, samuti reaktsioonikeskkonna elektrijuhtivusele.

Койт ЛЭЭТС

О МОДЕЛИ КИНЕТИКИ КАТИОННОЙ ТЕЛОМЕРИЗАЦИИ

Составлены кинетические и конверсионные уравнения катионной теломеризации, учитывающие изменения химической природы и реакционной способности активированных интермедиатов реакции при переходе от поляризованных (неионных) монокатогенных частиц к политаксогенным ионным частицам, а также изменения молекулярной массы и реакционной способности последних при росте цепи теломеризации.

Кинетика конверсии компонентов в ординарной системе теломеризации описывается следующим образом:

для телогена

$$\frac{dx_i}{dt} = \frac{[K_0] \bar{r}_j y_j (a_i x_i + b_j y_j)}{\left\{ \frac{\bar{r}_s s}{x_i} + 1 + \bar{r}_j y_j \left(1 + \frac{b_j y_j}{q_i x_i - \frac{1-\nu}{\nu} p_j y_j} \right) \right\}} = U$$

для таксогена

$$\frac{dy_j}{dt} = -[K_0] \bar{r}_j y_j \left[a_i x_i + b_j y_j \left(2 + \frac{p_j y_j}{q_i x_i} \right) \right] : U,$$

для получаемого моноаддукта

$$\frac{dz_{ij}}{dt} = [K_0] \bar{r}_j y_j a_i x_i : U,$$

где концентрации: $[K_0]$ — катализатора, x_i — телогена, y_j — таксогена, z_{ij} — моноаддукта, s — нуклеофильных лигандов; константы равновесия комплексов катализатора и телогена: \bar{r}_j — с монокатогенными активированными интермедиатами реакции, \bar{r}_s — с нуклеофильными лигандами среды; константы скорости а) монокатогенного интермедиата: a_i — с телогеном, b_j — с таксогеном, б) дитаксогенного интермедиата: q_i — с телогеном, p_j — с таксогеном; ν — константа снижения реакционной способности политаксогенной частицы при удлинении цепи ее молекулы на единицу таксогена.

Новая модель кинетики хорошо интерпретирует влияние электрофильности катализаторов и соотношения ингредиентов на состав продуктов и кинетику реакции, на изменения электропроводимости реакционной среды.