

A NOVEL METHOD FOR SYNTHESIZING ALKOXY-2-ALKENALS

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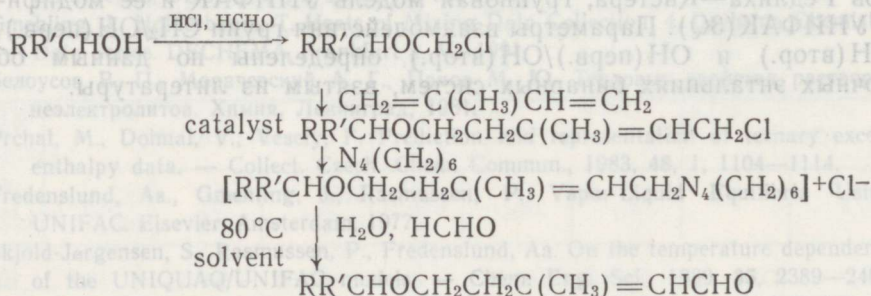
Abstract. A modified method and a new laboratory apparatus for synthesizing 3-methyl-5-alkoxy-2-alkenals from alkoxyallylic chlorides via quaternary salts with hexamethylenetetramine (the Sommelet reaction) was developed. The synthesis was carried out at 80 °C through the continuous extraction, with an organic solvent, of the product formed in the reaction mixture. This enabled to obtain unstable, in certain conditions, alkoxyalkenals.

Key words: aldehydes, 3-methyl-5-alkoxy-2-alkenals, alkoxyallylic chlorides, Sommelet reaction.

INTRODUCTION

Alkoxyaldehydes have been synthesized by Jarolim and Sorm from alcohols, vinylketones and diethylethoxycarbonylmethanephosphonate or ethoxycarbonylmethylenetriphenylphosphorane via oxacids and oxalcohols [1, 2]. Syntheses of alkoxyallylic chlorides from chloromethylethers and alkadienes are known [3], as well as a method for synthesizing 2-alkenals from allylic chlorides by the Sommelet reaction, for example, obtaining citral from geranylchloride over quaternary ammonium salt with hexamethylenetetramine by distillation with water steam in the presence of methanal [4].

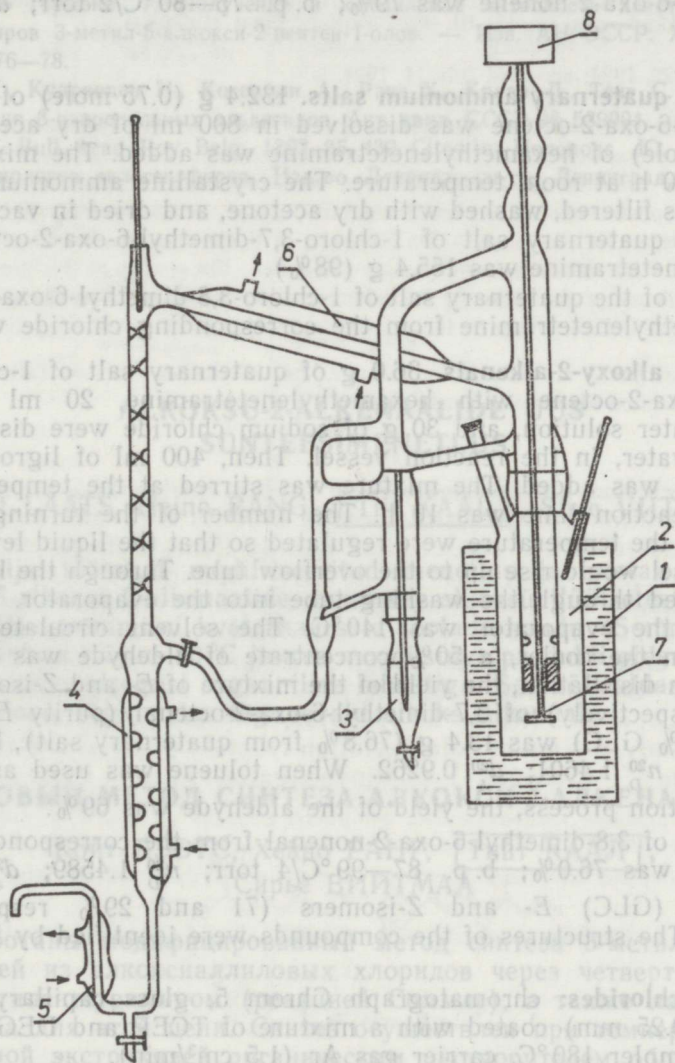
We have found that alkoxy-2-alkenals are not formed by distillation with water steam from a solution of quaternary ammonium salts of alkoxyallylic chlorides with hexamethylenetetramine. Therefore, we have developed a novel extraction process for the preparation of alkoxy-2-alkenals from alkoxyallylic chlorides. The synthesis of alkoxy-2-alkenals from alcohols and alkadienes is carried out according to the following scheme:



Here, R and R' are H or alkylgroups.

APPARATUS

The apparatus used to prepare alkoxy-2-alkenals from quaternary ammonium salts of alkoxyallylic chlorides with hexamethylenetetramine is shown in the Figure. The water solution of quaternary salt and solvent — ligroine (b. p. 110—120°C) or toluene — was added into the reaction vessel (2) in a thermostated bath (1). By stirring in the upper part of the reaction vessel, the solvent phase was separated and transferred into the evaporator (4) through the washing tube (3), filled with 3% sulfuric acid. From the evaporator, the vapour of the solvent was condensed in the condenser (6), and the liquid solvent was transferred into the lower part of the reaction vessel. From the lower part of the evaporator, the concentrate of the aldehyde was obtained through the cooler (5).



The apparatus for the synthesis and extraction of the alkoxy-2-alkenals from quaternary salts: 1 — thermostated bath, 2 — reaction vessel, 3 — washing tube, 4 — evaporator, 5 — cooler of the concentrate of aldehyde, 6 — condenser of the vapours of the solvent, 7 — agitator, 8 — electromotor.

Chloromethylethers were prepared in a manner similar to that described by Henry in [5].

Addition of chloromethylethers to isoprene. 0.5 ml of 5% solution of tin tetrachloride in dichloroethane was added to a mixture of 108.5 g (1 mole) of chloromethyl isopropyl ether, 68 g (1 mole) of isoprene, 100 ml of hexane, while stirring. The reaction temperature was 20–22°C, the reaction time 1 h. Then, 5 g of carbamide was added, the mixture was stirred for 15 min and filtered off. The unreacted substances were evaporated and the monoadduct was distilled from the residue at 69–75°C/5 torr; d_4^{20} 0.9491; n_D^{20} 1.4544. The yield of 1-chloro-3,7-dimethyl-6-oxa-2-pentene was 140.2 g (80%). From 1-chloro-4-methyl-2-oxa pentane the yield of 1-chloro-3,8-dimethyl-6-oxa-2-nonene was 79%; b. p. 75–80°C/2 torr; d_4^{20} 0.9414; n_D^{20} 1.4531.

Synthesis of quaternary ammonium salts. 132.4 g (0.75 mole) of 1-chloro-3,7-dimethyl-6-oxa-2-octene was dissolved in 800 ml of dry acetone, and 70 g (0.5 mole) of hexamethylenetetramine was added. The mixture was stirred for 10 h at room temperature. The crystalline ammonium quaternary salt was filtered, washed with dry acetone, and dried in vacuum. The yield of the quaternary salt of 1-chloro-3,7-dimethyl-6-oxa-2-octene with hexamethylenetetramine was 155.4 g (98%).

The yield of the quaternary salt of 1-chloro-3,8-dimethyl-6-oxa-2-nonene with hexamethylenetetramine from the corresponding chloride was 99%.

Synthesis of alkoxy-2-alkenals. 36.0 g of quaternary salt of 1-chloro-3,7-dimethyl-6-oxa-2-octene with hexamethylenetetramine, 20 ml of 37% methanal water solution, and 30 g of sodium chloride were dissolved in 300 ml of water, in the reaction vessel. Then, 400 ml of ligroine (b. p. 110–120°C) was added. The mixture was stirred at the temperature of 80°C, the reaction time was 10 h. The number of the turnings of the agitator and the temperature were regulated so that the liquid level in the reaction vessel would rise up to the overflow tube. Through the latter, the solvent passed through the washing tube into the evaporator. The temperature of the evaporator was 140°C. The solvent circulated in the system. From the cooler, a 50% concentrate of aldehyde was obtained. After vacuum distillation, the yield of the mixture of *E*- and *Z*-isomers (70 and 30% respectively) of 3,7-dimethyl-6-oxa-2-octenal (purity *E*- and *Z*-isomers 97.1% GLC) was 13.4 g (76.8% from quaternary salt), b. p. 71–80°C/3 torr; n_D^{20} 1.4601; d_4^{20} 0.9262. When toluene was used as solvent in the extraction process, the yield of the aldehyde was 69%.

The yield of 3,8-dimethyl-6-oxa-2-nonenal from the corresponding quaternary salt was 76.0%; b. p. 87–99°C/4 torr; n_D^{20} 1.4589; d_4^{20} 0.9174. The purity (GLC) *E*- and *Z*-isomers (71 and 29% respectively) was 97.9%. The structures of the compounds were identified by NMR ^{13}C spectra.

GLC of chlorides: chromatograph Chrom 5, glass capillary column (41 m, i. d. 0.25 mm) coated with a mixture of TCEP and DEGS (4:1) at 100°C, sampler 180°C, carrier gas Ar (1.5 cm³/min).

GLC of aldehydes: glass capillary column (47 m, i. d. 0.3 mm) coated with phenyldiethylamine succinate at 150°C, sampler 250°C, carrier gas Ar (1.5 cm³/min).

NMR spectra were measured from CDCl₃ solutions on a Bruker AM-500 spectrometer.

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ALKOKSÜ-2-ALKENAALIDE UUS SÜNTEESIMENETLUS

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On välja töötatud modifitseeritud menetlus ja vastav laboriseade 3-metüül-5-alkoksü-2-alkenaalide saamiseks alkoksüallüülsetest kloriididest heksametüleentetramiini kvaternaarse te soolade kaudu (Sommelet' reaktsioon). Süntees toimus 80°C juures moodustuva produkti pideval ekstrakt-sioonil reaktsioonisegust orgaanilise lahustiga. See võimaldas saada tunn- tud reaktsioonitingimustes lagunevaid alkoksüalkenaale.

НОВЫЙ МЕТОД СИНТЕЗА АЛКОКСИ-2-АЛКЕНАЛЕЙ

Койт ЛЭЭТС, Хейно РАНГ, Тийт КААЛ,
Сирье ВИЙТМАА

Разработаны модифицированный метод синтеза 3-метил-5-алкокси-2-алкеналей из алкоксиаллиловых хлоридов через четвертичные соли с гексаметилентетрамином (реакцией Соммле), а также лабораторная аппаратура для этой цели. Синтез осуществлен при температуре 80°C непрерывной экстракцией органическим растворителем образующегося из реакционной смеси продукта. Это позволило получить нестойкие в известных реакционных условиях алкоксиалкенали.

KINETIC MODEL OF THE ELECTROPHILIC HALOALKYLATION AND TELOMERIZATION OF ALKENES. THE DILUTION EFFECT

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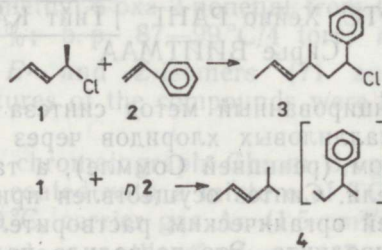
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Abstract. In the haloalkylation and telomerization reactions of styrene with 4-chloro-2-pentene in the presence of FeCl_3 a relative increase in the content of polyadducts, the so-called *negative dilution effect*, was observed when the concentrations of reagents were decreased. This phenomenon was absent when SnCl_4 was used as a catalyst. A new kinetic model is suggested for the reaction. On the basis of this model, the values of the relative kinetic constants for elemental reactions are calculated. The results of this study enable to find the dependence of the ratios of the telomerization homologues on the electrophilicity of the catalysts and to interpret the stereoselectivity of some haloalkylation reactions.

Key words: alkenes, styrene, chloroalkenes, haloalkylation, telomerization, catalysis electrophilic, reaction kinetic and mechanism.

The correlation of the composition of the electrophilic haloalkylation and telomerization products and reaction kinetics with reaction conditions has been studied on the reactions of 1,3-alkadienes with allylic [1,2] and alkoxyethyl [3,4] chlorides. In previous experiments, Lääts [5,6] has established that the haloalkylation of alkenes by the Lewis acid proceeds via two reaction intermediates: the coordination complex of the catalyst and ingredients, and the carbenium cation formed. The former afford the mono-adduct RYX . On the chain telomerization of the carbenium ion poly-adducts RY_nX , $n \geq 2$ (RX — alkyl halide, Y — alkene) are obtained.

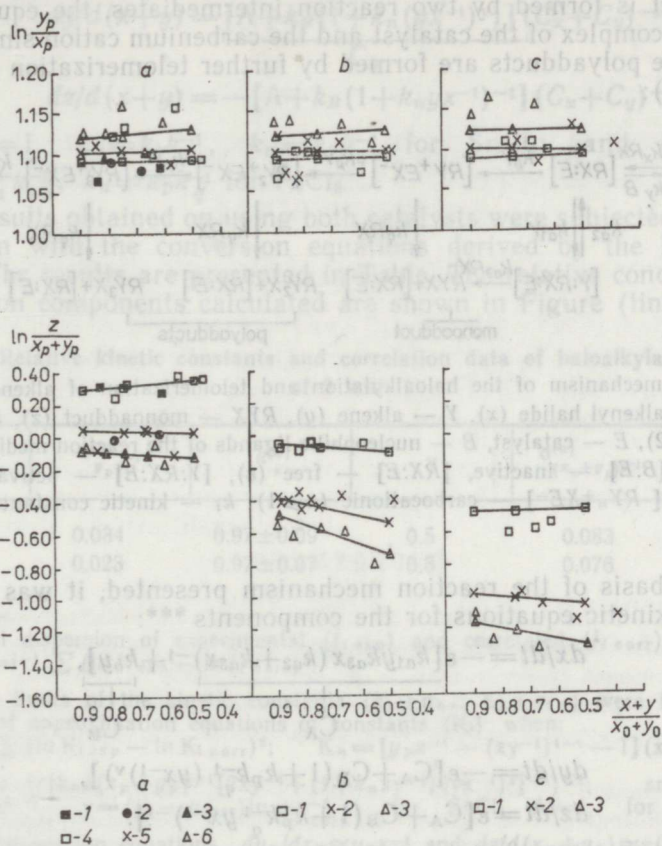
In this study, a simpler haloalkylation reaction of styrene with 4-chloro-2(*E*)-pentene [7] (Scheme 1) was investigated*:



* The absence of continued haloalkylation reactions of the primary adducts 3 and 4 with 1 and 2 was established by means of the competing reactions [8,9] of 1 and 1-chloro-1-phenylethane with 2, and of 2 and *E*-2-pentene with 1 by SnCl_4 and FeCl_3 by GLC analysis of the products obtained.

To establish quantitative relationships between the monohaloalkylation and telomerization reactions, the conversion model [10] was used. The dependence of the concentration of the reaction components on the initial concentrations of x_0 , and y_0 , the molar ratio xy^{-1} , the conversion degree $(x+y)(x_0+y_0)^{-1}$ and the electrophilicity of the catalyst FeCl_3 and SnCl_4 has been found.

The concentration of catalysts (10^{-4} – 10^{-3} mol·dm $^{-3}$) does not influence the composition of the products formed at the same conversion degree of ingredients. The experimental conditions and results are presented in Figure.



Catalysts SnCl_4 (a) and FeCl_3 (b, c). Experimental (points), and correlated (lines) data of the reaction of 2 with 1. Reaction conditions and procedures: temperature 289 ± 1 K, time 0.3–3.0 h; solvent *n*-hexane; 1,2-dichloroethane 2:1 by vol**. Concentrations, mol·dm $^{-3}$: catalyst 10^{-4} – 10^{-3} , reaction components x-1, y-2, z-3; conversion of 1 in 4 $x_p = x_0 - x - z$, of 2 in 4 $y_p = y_0 - y - z$.

a: $x_0 = 0.7$, $y_0 x_0^{-1} = 1.0$ (1), 1.5 (2), 2.0 (3); $x_0 = 1.8$, $y_0 x_0^{-1} = 1.0$ (4), 1.5 (5), 2.0 (6).

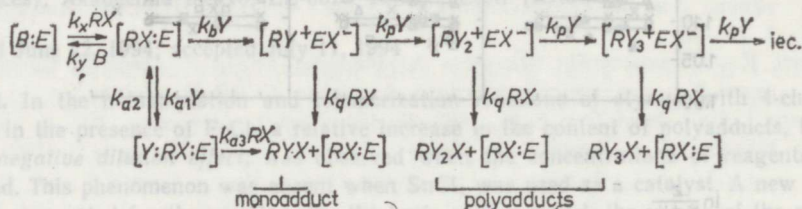
b: $x_0 = 1.8$, $y_0 x_0^{-1} = 1.0$ (1), 1.5 (2), 2.0 (3).

c: $x_0 = 0.7$, $y_0 x_0^{-1} = 1.0$ (1), 1.5 (2), 2.0 (3).

** Catalysts are added in chlorosolvent solutions and extracted by ethylene glycol, then dried on CaCl_2 . The concentrations of the monoadduct (z) and polyadducts (x_p , y_p) were determined by the distillation of the reaction products in vacuo (3 b.p. 115–130 °C at 5 mm) and elemental analysis of 4. The residual amounts of 2 in 3 and 3 in 4 were determined by GLC analysis of the products, using the internal standards: chlorobenzene for 2 and biphenyl for 3. GLC conditions: 1,2,3-tris(2-cyano-ethoxy)propane packed 24 m glass capillary column with FID, 40 °C for 2, 120 °C for 3.

The molar ratio of the ingredients in polyadducts depends little on the reaction conditions ($y_p x_p^{-1} = 2.95 : 3.15$). The relative rate $(x_p + y_p) z^{-1}$ increases when the molar ratio $y x^{-1}$ and electrophilicity of the catalyst ($\text{FeCl}_3 > \text{SnCl}_4$) are increased. At the same time, the ratio of the polyadducts formed by catalysis with SnCl_4 to monoadducts $(x_p + y_p) z^{-1}$ does not depend on the absolute concentration of the starting compounds (x_0 , Figure, a). In contrast to the catalyst SnCl_4 , with decreasing concentration of the ingredients (x_0, y_0 , Figure, b, c), the relative rate of the formation of polyadducts $(x_p + y_p) z^{-1}$ increases in case of FeCl_3 . Provisionally, this phenomenon might be called the *negative dilution effect*.

With the haloalkylation kinetics established, it can be assumed that a monoadduct is formed by two reaction intermediates, the equilibrium coordination complex of the catalyst and the carbenium cation simultaneously formed. The polyadducts are formed by further telomerization of the latter (Scheme 2):



The reaction mechanism of the haloalkylation and telomerization of alkenes. Concentrations: RX — alkenyl halide (x), Y — alkene (y), RYX — monoadduct (z), RY_nX — polyadducts ($n \geq 2$), E — catalyst, B — nucleophilic ligands of the reaction medium; complexes of catalyst: $[B:E]$ — inactive, $[RX:E]$ — free (ϵ), $[Y:RX:E]$ — activated reversible coordination, $[RY_n^+ XE^-]$ — carbocationic ($n \geq 1$); k_i — kinetic constants.

On the basis of the reaction mechanism presented, it was possible to derive the kinetic equations for the components***:

$$\begin{aligned}
 dx/dt &= -\epsilon \frac{k_{a1} y k_{a3} x (k_{a2} + k_{a3} x)^{-1} + k_b y}{C_A C_B}, \\
 dy/dt &= -\epsilon [C_A + C_B (1 + k_p k_q^{-1} (y x^{-1})^v)], \\
 dz/dt &= \epsilon [C_A + C_B (1 + k_p k_q^{-1} y x^{-1})^{-1}].
 \end{aligned}$$

From the above kinetic equations, it may be concluded that if $k_{a2} \ll k_{a3} x$, the limiting stage in the partial reaction of the coordination complex is the formation of the reaction intermediate and $C_A \rightarrow k_{a1} y$. At the same time, partial reaction orders become equal $C_A = k_B C_B$ ($k_B = k_b k_{a1}^{-1}$), and the relative rate of the formation of the products obtained by different mechanisms does not depend on the absolute concentrations of x_0 and y_0 . That is consistent with the experimental data obtained on catalysis with SnCl_4 (Figure, a).

If $k_{a2} \gg k_{a3} x$, the limiting stage in the above partial reaction is the removal of the catalyst from the coordination complex and $C_A \rightarrow k_{a1} k_{a3} k_q^{-1} x y$. In the latter case, the relative rate of the partial cationic

*** For the designations of concentrations and kinetic constants, see Scheme 2; v — an empirical exponent expressing the average relationship between the relative rates of telomerization chain propagation and transfer by an increase in the molar mass of RY_n^+ .

reaction and the formation of polyadducts depends inversely on the concentration of the initial halogenide: $C_B C_A^{-1} = k_B x^{-1}$ ($k_B = k_b k_{a2} k_{a1}^{-1} k_{a3}^{-1}$). That is consistent with the experimental data obtained on catalysis with $FeCl_3$ (Figure, b, c).

On substituting, in the kinetic equations, the above approximations for the C_A , and the changes in the concentration of the initial compounds for the time argument, the simplified differential conversion equations [10] will be obtained:

$$dx/d(x+y) = \frac{[A+k_B](C_x+C_y)^{-1}}{C_x}$$

$$dy/d(x+y) = \frac{[A+k_B(1+k_n(yx^{-1})^v)](C_x+C_y)^{-1}}{C_y}$$

$$dz/d(x+y) = -[A+k_B(1+k_n yx^{-1})^{-1}](C_x+C_y)^{-1},$$

when $A=1$, $k_B = k_b k_{a1}^{-1}$, $k_n = k_p k_q^{-1}$ for $SnCl_4$; and $A=x$, $k_B = k_b k_{a2} k_{a1}^{-1} k_{a3}^{-1}$, $k_n = k_p k_q^{-1}$ for $FeCl_3$.

The results obtained on using both catalysts were subjected to computer correlation with the conversion equations derived by the least squares method. The results are presented in Table. The relative concentrations of the reaction components calculated are shown in Figure (lines).

Relative kinetic constants and correlation data of haloalkylation of 2 with 1

Catalyst	$\sigma_{y_p x_p^{-1}}^{(a)}$	$k_n^{(b)}$	ν	$\sigma_{(x_p+y_p)z^{-1}}^{(a)}$	$k_B^{(b)}$
$SnCl_4$	0.034	0.97 ± 0.09	0.5	0.083	0.48 ± 0.08
$FeCl_3$	0.023	0.97 ± 0.07	0.5	0.076	1.40 ± 0.20

(a) Residual dispersion of experimental ($f_{i \text{ exp}}$) and correlated ($f_{i \text{ corr}}$) data was calculated $\sigma_f^2 = i^{-1} \sum (\ln f_{i \text{ exp}} - \ln f_{i \text{ corr}})^2$.

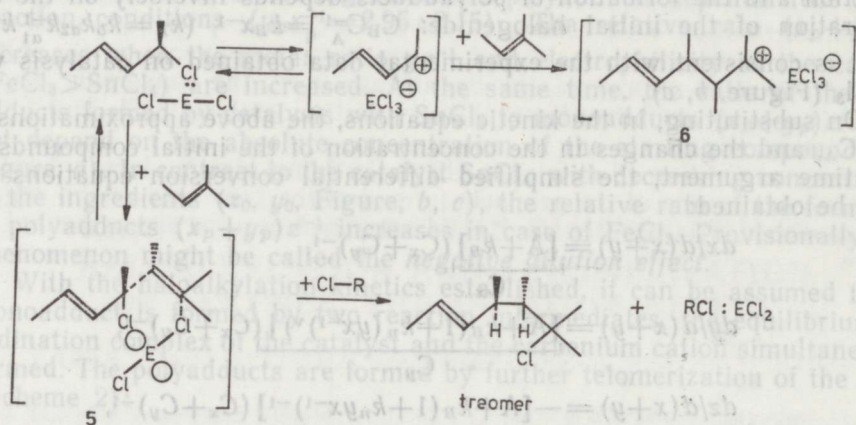
(b) Validity limits of the kinetic constants ($k_n \pm \sigma_{k_n}$; $k_B \pm \sigma_{k_B}$) were found from the dispersions of approximation equations of constants (K_i) when:

$\ln^2 \sigma_{k_n} = i^{-1} \sum (\ln K_{i \text{ exp}} - \ln K_{i \text{ corr}})^2$; $K_n = [y_p x_p^{-1} - (xy^{-1})^{1-\nu} - 1](xy^{-1})^\nu$; $K_B = \frac{A(1+k_n yx^{-1})\{k_n z(x_p+y_p)^{-1}[2xy^{-1} + (1+k_n xy^{-1})(yx^{-1})^\nu]^{-1}\}^{-1}}{(x_0 - x_{\text{corr}}) \ln x_0 x_{\text{corr}}^{-1}}$; $y = (y_0 - y_{\text{corr}}) \ln y_0 y_{\text{corr}}^{-1}$; for $SnCl_4$ $A=1$, for $FeCl_3$ $A=x$.

Taking, in conversion equations, $dy_p/dx_p \cong y_p x_p^{-1}$ and $dz/d(x_p+y_p) \cong z(x_p+y_p)^{-1}$, for the experimental conditions used the calculated square error $(K_i k_i^{-1} - 1)^2 \cong 2 \cdot 10^{-4}$.

It follows from the correlation results and the relative rate constant values found that by a partial carbocationic reaction (telomerization) the selectivity relative to chain propagation and transfer is absent ($k_n \cong 1$). With the increasing molar mass of the carbenium cation RY_n^+ , the relative chain propagation rate decreases ($\nu=0.5$). With increasing electrophilicity of the catalyst ($FeCl_3 > SnCl_4$) the relative rate of the partial carbocationic reaction and simultaneous polyadducts formation increases (k_B 0.46 \rightarrow 1.4). At the same time, the partial reaction order decreases, leading to the observed *dilution effect* on catalysis by $FeCl_3$.

On the basis of the reaction mechanism studied, a cyclic structural formula of the coordination complex intermediate might be proposed (shown in Scheme 3). This enabled us to interpret the diastereoselectivity by haloalkylation of some substituted isoalkenes.



Stereospecific cyclic 5 and nonselective carbocationic 6 haloalkylation reaction complexes of 2-methyl-2-butene with 4-chloro-2-butene (treomer:erythromer=2:1, $ECl_2 = SnCl_4$ [11-13]).

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ALKEENIDE ELEKTROFIILSE HALOALKÜLEERIMISE JA TELOMERISATSIOONI KINEETIKA MUDEL. LAHJENDUSEFEKT

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Stüreeni haloalküleerimisel 4-kloro-2-penteeniga FeCl_3 manulusel tuvas-tati polüaduktide suhtelise sisalduse suurenemine lähteainete kontsentratsioonide vähenemisel — *negatiivne lahjendusefekt*. Viimast ei täheldatud SnCl_4 kasutamisel katalüsaatorina.

Tuletati uus reaktsioonikineetika mudel, mille alusel arvutati osareaktsioonide suhteliste kiiruskonstantide väärtused. Uurimistulemused võimaldasid leida sõltuvuse telomerisatsiooniproductide homoloogilise koostise ja katalüsaatorite elektrofiilsuse vahel.

КИНЕТИКА ЭЛЕКТРОФИЛЬНОГО ГАЛОАЛКИЛИРОВАНИЯ И ТЕЛОМЕРИЗАЦИИ АЛКЕНОВ. ЭФФЕКТ РАЗБАВЛЕНИЯ

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При галоалкилировании стирола с 4-хлор-2-пентеном в присутствии FeCl_3 установлен *отрицательный эффект разбавления*, т. е. увеличение относительного содержания полиаддуктов при снижении концентрации ингредиентов. Разработана новая кинетическая модель реакции и на ее базе рассчитаны значения для относительных кинетических констант элементарных реакций. Результаты работы позволили найти связь между гомологическим составом теломеров и электрофильностью катализаторов, а также интерпретировать стереоселективность некоторых реакций галоалкилирования.