

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

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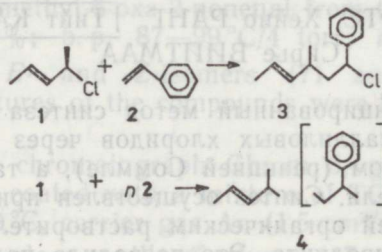
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Abstract. In the haloalkylation and telomerization reactions of styrene with 4-chloro-2-pentene in the presence of FeCl_3 a relative increase in the content of polyadducts, the so-called *negative dilution effect*, was observed when the concentrations 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.

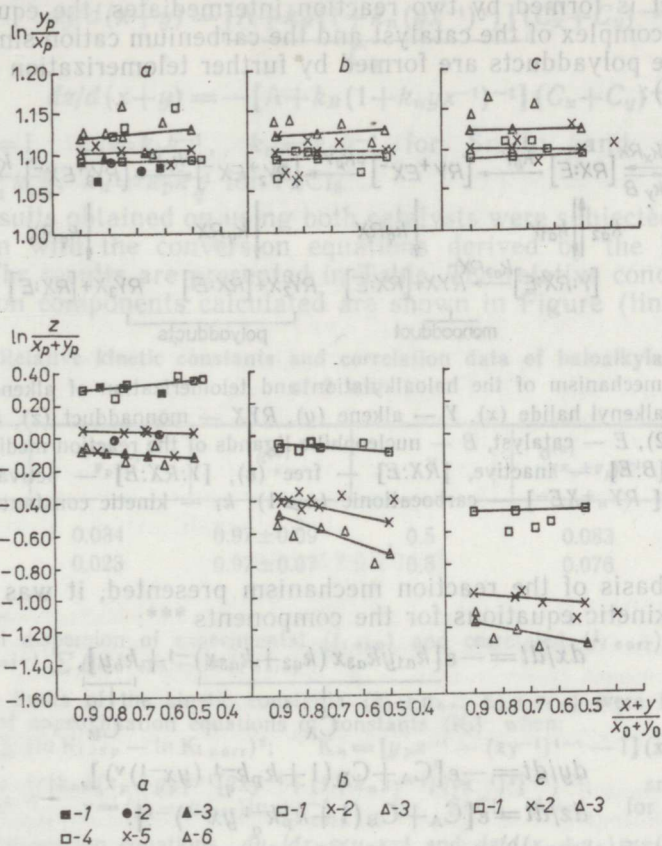
In this study, a simpler haloalkylation reaction of styrene with 4-chloro-2(*E*)-pentene [7] (Scheme 1) was investigated*:



* 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).

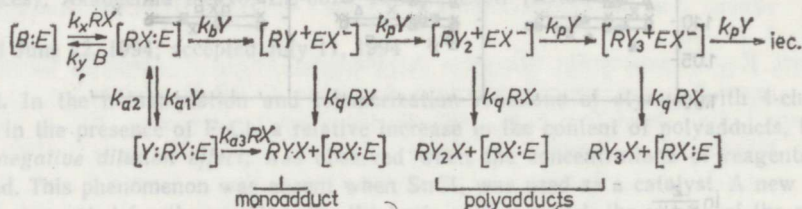
b: $x_0 = 1.8$, $y_0 x_0^{-1} = 1.0$ (1), 1.5 (2), 2.0 (3).

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 $C_A \rightarrow k_{a1} k_{a3} k_{a2}^{-1} x y$. 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 $\sigma_f^2 = i^{-1} \sum (\ln f_{i \text{ exp}} - \ln f_{i \text{ corr}})^2$.

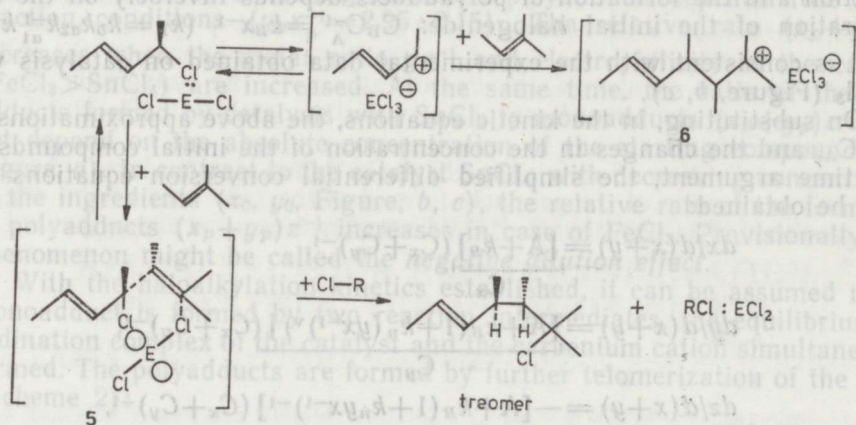
(b) Validity limits of the kinetic constants ($k_n \pm \sigma_{k_n}$; $k_B \pm \sigma_{k_B}$) were found from the dispersions of approximation equations of constants (K_i) when:

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

Койт ЛЭЭТС, Малле ШМИДТ, Маре ХЕЙНВЯЛИ,
Ильмар КИРЬЯНЕН

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.