

Dedicated to the 100th anniversary of
Paul Nikolai Kogerman's birth

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ON THE THERMOPOLYMERIZATION MECHANISM AND KINETICS OF 1,4- AND 1,5-ALKADIENES

Abstract. A correlation analysis of the results of P. N. Kogerman's study of the adducts composition of the thermopolymerization of 1,4-pentadiene and 1,5-hexadiene as well as of the reaction kinetics of 1,4-pentadiene was carried out. It was found that the above reactions proceed according to the chain telomerization mechanism. The corresponding reaction kinetics equations were constructed. By means of these equations the relative rate constants and also the reaction activation parameters for 1,4-pentadiene thermopolymerization were calculated.

Of P. N. Kogerman's investigations of dienes, their thermopolymerization chemism and kinetics are of the greatest scientific interest.

The thermal dimerization of 2,3-dimethyl-1,3-butadiene was pointed out by I. Kondakow already in 1890 [1]. The chemical structure of a dimer was proved by P. N. Kogerman in 1933 [2]. The thermopolymerization of 1,3-dienes has been established to be [4+2] cycloaddition accompanied by polymerization. Results of a study on the thermopolymerization chemism and kinetics of 1,4-penta- and 1,5-hexadienes were published by P. N. Kogerman in 1949 [3]. These reactions have been shown to proceed via primary isomerization of the starting dienes to the conjugated 1,3-pentadiene and 2,4-hexadiene (see Fig. 1). The [4+2] cycloaddition of the conjugated dienes with the isolated multiple bonds of the starting dienes affords dimers, and that with the multiple bonds of the dimers formed yields trimers. The higher adducts have also been found, supposedly copolymers of conjugated dienes with alkenes. In [3] experimental data on the change in the yield and composition of adducts in the reactions of 1,4-penta- and 1,5-hexadienes depending on temperature and process duration have been presented. It has been found that in many steps the kinetics of ingredients conversion obeys firstorder reaction while with progressing conversion the reactions are cycled. It has also been established that the thermal and the catalytic isomerization of 1,4- and 1,5-dienes in conjugated dienes are irreversible. However, no significant amounts of intermediate conjugated 1,3- and 2,4-alkadienes have been detected in thermopolymerization mixtures.

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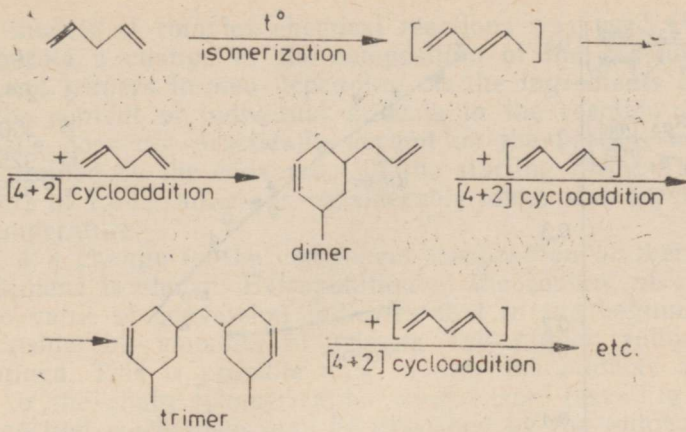


Fig. 1. Scheme for the thermopolymerization of 1,4-pentadiene [3].

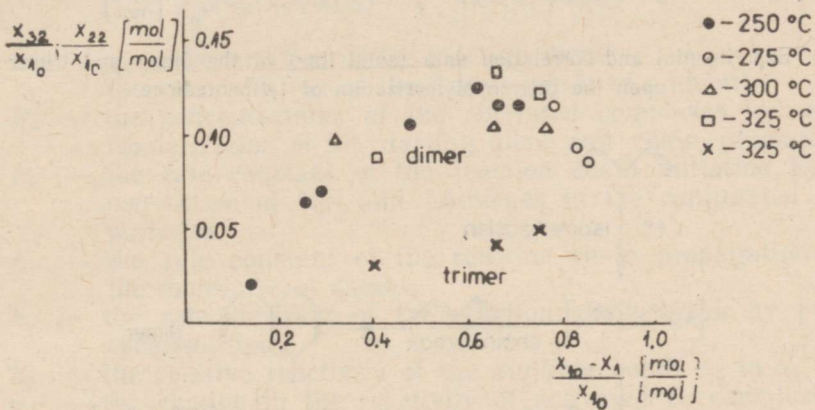


Fig. 2. Conversion of 1,4-pentadiene (x_1) to dimer (x_{22}) and trimer (x_{32}); x_{10} is the starting concentration of x_1 .

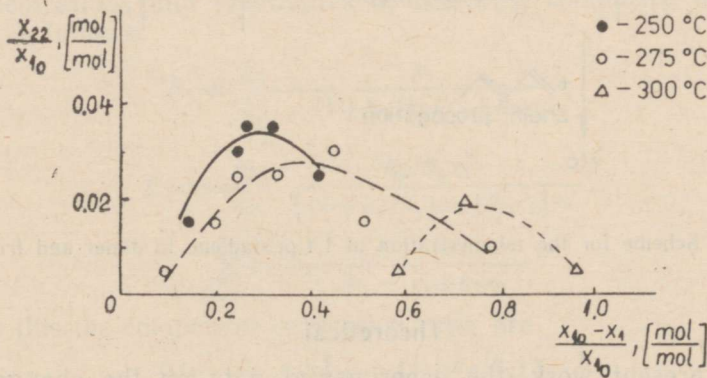


Fig. 3. Conversion of 1,5-hexadiene (x_1) to dimer (x_{22}); x_{10} is the starting concentration of x_1 .

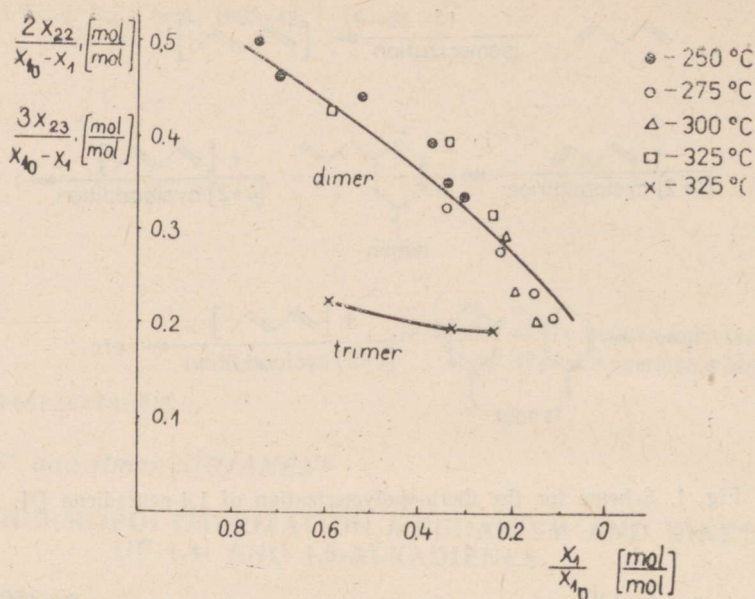


Fig. 4. Experimental and correlation data (solid line) of the dimer and trimer formed upon the thermopolymerization of 1,4-pentadiene.

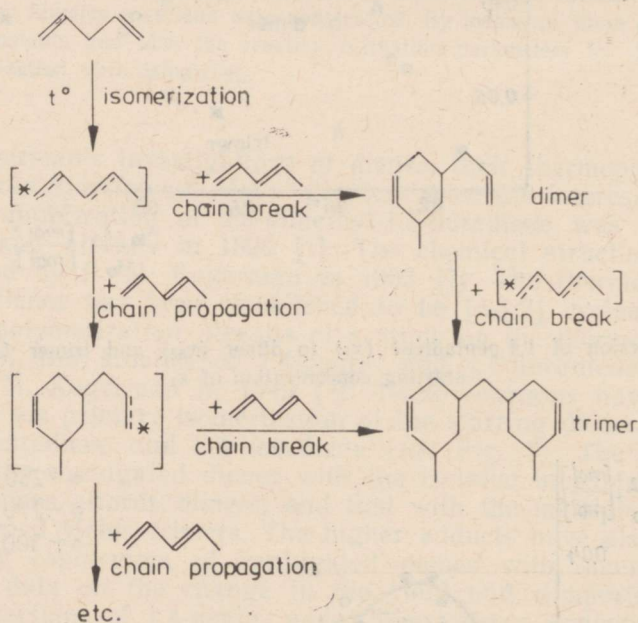


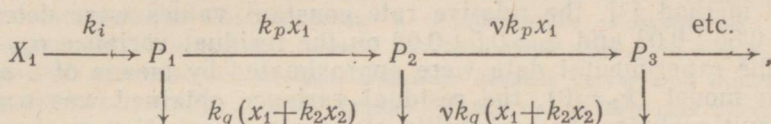
Fig. 5. Scheme for the telomerization of 1,4-pentadiene to dimer and trimer.

Theoretical

In the present work, the experimental data on the change in the composition of thermopolymerization products of 1,4- and 1,5-alkadienes, as well as the reaction kinetics presented in [3] were subjected to correlation analysis. To obtain preliminary information about possible kinetic schemes of the reactions under study, a method of constructing

conversion models of complex chemical reactions was used [4]. Figs. 2 and 3 illustrate a change in the composition of the reaction mixture of dimers and trimers formed depending on the ingredients conversion. As seen, the content of individual adducts in the reaction mixture of 1,4-pentadiene does not practically depend on the process temperature and is determined by the conversion of the starting diene. The yield of thermodimers of 1,5-hexadiene is considerably lower and depends on the reaction temperature.

In Fig. 4 a change in the component composition of thermoadducts of 1,4-pentadiene is shown. Extrapolation of the content of components to the zero value of conversion indicates that in the beginning of the reaction considerable amounts of trimers and higher adducts should also be formed. This is possible only in case the adducts are formed according to the chain telomerization mechanism (see Fig. 5). The assumed reaction mechanism may be described by the following kinetic scheme:



- where x_1 — the concentration of the starting diene;
 x_2 — the concentration of the double bonds of adducts;
 P_i — the concentrations of the activated complexes formed by isomerization of the starting diene and chain propagation;
 k_i — the rate constant of the reaction chain initiation by isomerization of 1,4- and 1,5-dienes in the conjugated diene particles;
 k_p — the rate constant of the reaction chain propagation with the molecules of dienes;
 k_q — the rate constant of the reaction chain break by [4+2] cycloaddition;
 k_2 — the relative reactivity of the multiple bonds x_2 to x_1 ;
 ν — the change in the reactivity of activated P_i complexes in chain propagation by one diene unit.

Using the replacement

$$q = \frac{k_p x_1}{\nu [(k_p + k_q) x_1 + k_q k_2 x_2]}$$

the concentrations and reactivities of activated complexes may be expressed as follows:

$$\begin{aligned}
 P_1 &= \frac{k_i}{k_q} \frac{x_1}{(1 + k_p/k_q) x_1 + k_2 x_2}, \\
 P_2 \nu &= \frac{k_i}{k_q} \frac{k_p/k_q x_1^2}{[(1 + k_p/k_q) x_1 + k_2 x_2]^2}, \\
 \sum_{i=1}^{\infty} P_i \nu^i &= \frac{k_i}{k_q} \frac{x_1}{x_1 + k_2 x_2}.
 \end{aligned}$$

From this the component conversion rates are

$$\begin{aligned}
 \frac{dx_1}{dt} &= -k_i x_1 \left[1 + \frac{(1 + k_p/k_q) x_1}{x_1 + k_2 x_2} \right], \\
 \frac{dx_2}{dt} &= k_i x_1 \left[1 + \frac{(1 + k_p/k_q) x_1}{x_1 + k_2 x_2} \right],
 \end{aligned}$$

$$\frac{dx_{22}}{dt} = k_i x_1 \left[\frac{x_1}{(1+k_p/k_q)x_1+k_2x_2} - \frac{2k_2x_{22}}{x_1+k_2x_2} \right],$$

$$\frac{dx_{32}}{dt} = k_i x_1 \left[\frac{2k_2x_{22}}{(1+k_p/k_q)x_1+k_2x_2} + \right.$$

$$\left. + \frac{k_p/k_q x_1^2}{[(1+k_p/k_q)x_1+k_2x_2]^2} - \frac{2k_2x_{32}}{x_1+k_2x_2} \right],$$

where x_{22} — the concentration of a dimer,
 x_{32} — the concentration of a trimer.

The kinetic equations derived were transformed into the conversion equations of the reaction components dx_i/dx_1 [4]. By approximating the conversion solutions with the experimental data [3] using the least squares method [5], the relative rate constant values were determined: $k_p/k_q = 0.55 \pm 0.03$ and $k_2 = 0.5 \pm 0.02$ on the residual variance $\sigma_{av} = 0.055$. When the experimental data were approximated by means of a stepwise addition model ($k_p = 0$), the residual variance obtained was $\sigma_{av} = 0.36$. This result excludes the probability of a stepwise reaction mechanism.

The values of k_p/k_q and k_2 found in the conversion model were introduced into the kinetic equation of the starting diene. By approximation of the reaction times presented in [3], the reaction activation parameters were calculated: $\Delta H^\# = 36 \text{ kcal} \cdot \text{mol}^{-1}$; $\Delta S^\# = 28 \text{ cal} \cdot \text{mol}^{-1} \text{K}^{-1}$; on the residual variance of the experimental data $\sigma_{av} = 0.067$.

It was not possible to carry out a correlation analysis of the conversion data for 1,5-hexadiene as in [3] no yields of trimers have been given, and those of dimers at different temperatures are insufficient.

The thermopolymerization activation parameters found for 1,4-pentadiene are considerably higher than those of the reactions of conjugated dienes. For example, upon dimerization of a cyclopentadiene it was found to be $\Delta H^\# = 15.5 \text{ kcal} \cdot \text{mol}^{-1}$, $\Delta S^\# = 34 \text{ cal} \cdot \text{mol}^{-1} \text{K}^{-1}$ [6].

It should be pointed out that in order to specify the chemism and mechanism of the reactions studied, it is necessary to determine the structural composition of trimers and polymers and its change depending upon reaction conditions.

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1,4- JA 1,5-ALKADIEENIDE TERMOPOOLÜMERISATSIIONI MEHHAANISM JA KINEETIKA

On tehtud korrelatsioonanalüüs P. N. Kogermani poolt 1,4-pentadieeni ja 1,5-heksadieeni termopolümerisatsiooni reaktsioonide uurimisel saadud andmete kohta. On leitud, et reaktsioonid kulgevad aheltelomerisatsiooni mehhanismil, ning koostatud reaktsioonide kineetikavõrrandid, arvutatud katseandmetest suhtelised kiiruskonstandid ja täpsustatud reaktsioonide aktivatsiooniparameetrid.

Койт ЛЭЭТС, Ильмар КИРЬЯНЕН

МЕХАНИЗМ И КИНЕТИКА ТЕРМОПОЛИМЕРИЗАЦИИ 1,4- И 1,5-АЛКАДИЕНОВ

Проведен корреляционный анализ данных, полученных П. Н. Когерманом о реакциях термopolимеризации 1,4-пентадиена и 1,5-гексадиена. Установлено, что эти реакции протекают по механизму цепной теломеризации. Составлены соответствующие уравнения кинетики, по экспериментальным данным рассчитаны относительные константы скорости реакции, а также уточнены константы активизации реакции.