

# KINETICS OF THE ANIONIC COORDINATION DIMERIZATION OF ISOPRENE

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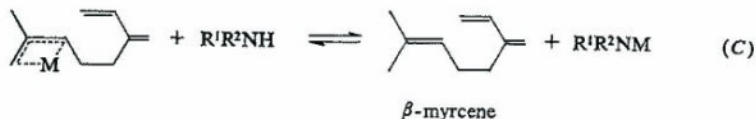
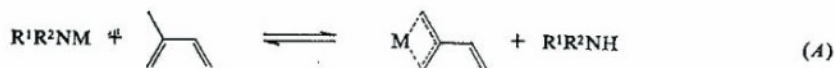
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The kinetics of the anionic coordination dimerization of isoprene (*i.e.*, 2-methyl-1,3-butadiene) to  $\beta$ -myrcene (*i.e.*, 7-methyl-3-methylene-1,6-octadiene) was investigated. The reaction was initiated with sodium in the presence of dicyclohexyl amine in tetrahydrofuran. Kinetic measurements showed that ionic pairs of isoprenyl sodium were additionally solvated by two molecules of tetrahydrofuran. A kinetic model of the reaction enabled the time dependence of the isoprene concentration to be expressed in terms of a two-parameter equation.

In our preceding paper<sup>1</sup> the mechanism of the anionic coordination dimerization of isoprene (*i.e.*, 2-methyl-1,3-butadiene) to  $\beta$ -myrcene (*i.e.*, 7-methyl-3-methylene-1,6-octadiene) has been suggested using the scheme (A)–(C):



M = Na, K

R<sup>1</sup>, R<sup>2</sup> = alkyl, cycloalkyl

For the sake of simplicity, the solvation effect of tetrahydrofuran in which the

reaction was carried out is not considered in the suggested reaction mechanism. The influence of possible association effects of organometallic compounds was also neglected. These effects, observed mainly in nonpolar solvents, have been discussed in detail in refs<sup>2-4</sup>. In this study the mechanism of the dimerization reaction (A)–(C) was used as the starting point for a kinetic model of the reaction, the solution of which provided a mathematical description of the conversion of isoprene to  $\beta$ -myrcene.

## EXPERIMENTAL

### Chemicals Used

Isoprene (I), tetrahydrofuran (THF), dicyclohexyl amine, sodium and nitrogen were purified as described in ref.<sup>1</sup>. The origin and purity of the chemicals also correspond to ref.<sup>1</sup>.

### Methods

In a 50 ml reactor with a magnetic stirrer, washed with nitrogen, equimolar amounts of sodium, isoprene and dicyclohexyl amine were mixed at room temperature against a stream of nitrogen in tetrahydrofuran in excess of several moles. The reactor containing a homogeneous initiation solution (c. 10 ml) formed after 30 min of the reaction was immersed into a bath 10°C. Isoprene was added in excess to the initiation solution against the stream of nitrogen, and the reaction system was thus obtained. The onset of the reaction ( $t = 0$ ) was defined by the addition of isoprene to the initiation solution. The initial rate of isoprene consumption was investigated as a function of the composition of the reaction system.

### Analytical Methods

The composition of the reaction mixture was analyzed by gas chromatography using a Chrom 4 apparatus (Laboratory Instruments, Prague) with flame-ionization detection. A packed glass column, 2.5 m long, inner diameter 2 mm, packing 15% Apiezon L and 3% NaOH on Chromaton N-AW-HMDS was used. The injected amount was 3  $\mu$ l of the reaction mixture, with nitrogen as the carrier gas. The temperature was program-controlled between 50°C–200°C with the temperature gradient 20°C/min and plateaus 2 min at 50°C and 12 min at 100°C. The nitrogen overpressure at the column inlet was 83–120 kPa. The isoprene and  $\beta$ -myrcene concentrations were determined by using calibration plots.

## RESULTS AND DISCUSSION

Two limiting cases of the course of the dimerization reaction of isoprene (I) according to scheme (A)–(C) have been considered. In the first case (I) the equilibrium (A) was supposed to be established instantaneously. In this case the rate of consumption of isoprene would be limited by the rate of addition according to relation (B). This procedure allowed us to explain the influence of tetrahydrofuran on the reaction course. In the second case (II) the back reaction of equilibrium (A) was neglected, further simplifying rearrangements were made and a kinetic model of the reaction

was obtained. Both these cases representing limits between which a real reaction course can be expected are discussed below.

### Kinetic Model I

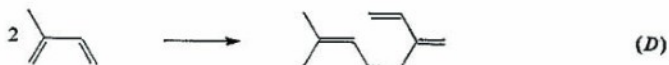
Within a broad time interval, the rate of isoprene consumption in the reaction systems under investigation (Table I) is independent of the instantaneous isoprene concentration (Fig. 1). Experiments have revealed that the initial rate of isoprene consumption,  $r_0$ , corresponds to the initial rate of the increase in  $\beta$ -myrcene determined as a tangent

TABLE I

Effect of the initial composition of the reaction system on the initial rate ( $r_0$ ) of isoprene consumption (I) and on the rate-determining parameters  $A$  and  $q$  (Eq. 19). The data are listed for series of identical initial molar ratios of the given reaction components (amine stands for dicyclohexylamine)

$(C_{\text{THF}})_0$	$(C_I)_0$	$C_{\text{Na}}$	$r_0 \cdot 10^3$ $\text{mol l}^{-1} \text{min}^{-1}$	$r_0 / (C_I)_0 \cdot 10^3$ $\text{min}^{-1}$	$A$	$q \cdot 10^3$ $\text{min}^{-1}$
$\text{mol l}^{-1}$						
(THF + I) : Na : amine = 26 : 1 : 1						
1.5	8.1	0.36	10	1.2	0.28	2.2
2.6	7.3	0.37	21	2.9	0.40	4.0
4.1	5.8	0.38	22	3.8	0.42	4.4
5.2	5.0	0.40	17	3.4	0.36	5.1
7.0	3.3	0.40	9	2.7	0.49	2.6
9.0	1.7	0.42	7	4.0	0.40	5.1
I : Na : amine = 13 : 1 : 1						
1.5	7.7	0.59	9	1.1	0.34	1.5
3.3	6.6	0.50	15	2.3	0.53	2.1
7.0	3.2	0.26	9	2.6	0.60	2.3
10.0	1.8	0.15	6	3.3	0.25	6.2
THF : Na : amine = 13 : 1 : 1						
1.7	8.5	0.13	9	1.1	0.13	4.2
3.4	6.8	0.26	20	2.9	0.34	4.2
6.9	3.3	0.53	9	2.6	0.56	2.3
8.9	1.6	0.68	6	3.7	0.87	2.0

to the curve representing the dependence of  $\beta$ -myrcene on time at a point  $t = 0$ , bearing in mind a change in the mol number in the reaction



Hence, it may be inferred that the concentration of intermediates in the reactions (A)–(C) is very low.

The dependence of the initial rate of isoprene consumption ( $r_0$  in  $\text{mol l}^{-1} \cdot \text{min}^{-1}$ ) on the initial concentration (in  $\text{mol l}^{-1}$ ) of the individual components of the reaction system ( $c_{\text{Na}}$  denotes the analytically determined sodium concentration) can be expressed through a formal kinetic equation

$$r_0 = 2.88 \cdot 10^{-4} (c_{\text{THF}})_0^{0.96} (c_1)_0^{1.59} c_{\text{Na}}^{0.16}, \quad (1)$$

where formal orders of magnitude of the individual components of the system and formal rate constants have been calculated by a multiple regression analysis of the linearized form of Eq. (1) with the correlation coefficient 0.86.

The effect of tetrahydrofuran on the reaction course can be explained by an additional solvation of ionic pairs  $\text{Na}^+ \text{C}_2\text{H}_5\text{C}(\text{CH}_3)=\text{CH}^-$  and  $\text{Na}^+ \text{C}_2\text{H}_5\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2^-$  with tetrahydrofuran according to (E), (F)

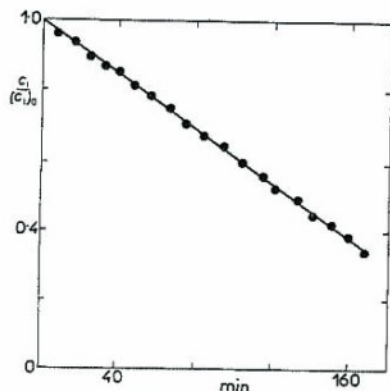
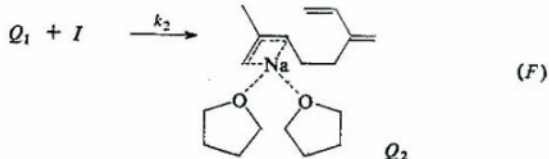
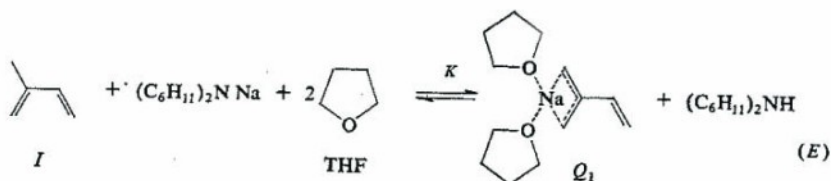


FIG. 1

Dimerization process of isoprene (*I*) in the system THF-dicyclohexylamine-Na-I; ( $c_I$ )<sub>0</sub> = 5.0 mol l<sup>-1</sup>,  $c_{Na}$  = 0.4 mol l<sup>-1</sup>, initial molar ratio THF : Na : dicyclohexylamine = 13 : 1 : 1





For the concentration of ionic pairs  $Q_1$  it can be written, assuming an instantaneous establishment of equilibrium (E),

$$c_{Q_1} = K^{0.5} (c_I)_0^{0.5} (c_{THF})_0 c_A^{0.5}, \quad (2)$$

where  $c_A$  is the concentration of sodium dicyclohexylamide; substitution of the initial isoprene and tetrahydrofuran concentrations instead of the equilibrium ones is a simplifying act due to the large excess of isoprene and tetrahydrofuran with respect to sodium dicyclohexylamide. Let it also be assumed that sodium is distributed only between the ionic pairs  $Q_1$  and sodium dicyclohexylamide, and that the relation

$$c_{Na} = c_{Q_1} + c_A \quad (3)$$

is valid. The rate of isoprene consumption is then limited by the addition of ionic pairs  $Q_1$  and isoprene (for a region close to the onset of the reaction, where isoprene in the reaction system markedly prevails by its concentration, and thus  $c_{Q_1} \gg c_{Q_2}$ ):

$$-d(c_I)_0/dt = r_0 = k_2 c_{Q_1} (c_I)_0 = k_2 K^{0.5} (c_{THF})_0 (c_I)_0^{0.5} c_A^{0.5}. \quad (4)$$

By comparing Eqs (1) and (4), we can see a perfect agreement in the reaction order to isoprene. The difference between the reaction order to Na (Eq. (1)) and sodium dicyclohexylamide (Eq. (4)) obviously follows from the fact that all sodium has not been distributed in the form of sodium dicyclohexylamide. Eq. (2) can namely be written as

$$c_{Q_1}^2 = K(c_I)_0 (c_{THF})_0^2 (c_{Na} - c_{Q_1})^2 \quad (5)$$

whence for the concentration  $c_{Q_1}$  we have

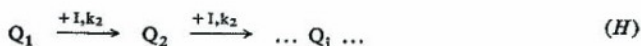
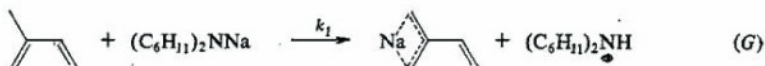
$$c_{Q_1} = P[(1 + 4c_{Na}/P)^{0.5} - 1]/2, \quad (6)$$

$$P = K(c_1)_0 (c_{THF})_0^2. \quad (7)$$

Only in the case where  $P$  is sufficiently small, Eq. (6) assumes the form of (2), and it holds that  $c_A \approx c_{Na}$ .

### Kinetic Model II

The kinetic model of a reaction in which for the sake of simplicity no additional solvation of pairs  $Q_1, Q_2 \dots Q_i$  with tetrahydrofuran is considered has been suggested using schemes (G), (H).



In the equilibrium (A) the reversible reaction had been neglected. The concentration of dicyclohexylamide has been found constant during the reaction. For this reason, and assuming that sodium is mainly distributed in the form of sodium dicyclohexylamide ( $c_A \gg \sum_i c_{Q_i}$ ), it can be written that

$$k_1 \cdot c_A = k'_1. \quad (8)$$

If, for simplicity's sake, we consider the rate constants of the addition of isoprene to ionic pairs  $Q_1, Q_2, \dots Q_i$  to be equivalent, for the dependence of the isoprene concentration and ionic pairs  $Q$  on time it can be derived that

$$-dc_I/dt = k_2 c_Q c_I + k'_1 c_I, \quad (9)$$

$$dc_Q/dt = k'_1 c. \quad (10)$$

For the dependence of the isoprene concentration on time it holds that

$$c_I = -2DC_2/k'_1 k_2 (e^{-\sqrt{(D)/2}t} - C_2 e^{+\sqrt{(D)/2}t})^2 \quad (11)$$

$$D = k_1'^2 + 2k_2 C_1, \quad (12)$$

where  $\dot{C}_1$ ,  $C_2$  are the integration constants. Eq. (11) can be advantageously rearranged to a two-parameter relation

$$c_1/(c_1)_0 = 1/(\cosh \varrho t + A \sinh \varrho t)^2 \quad (13)$$

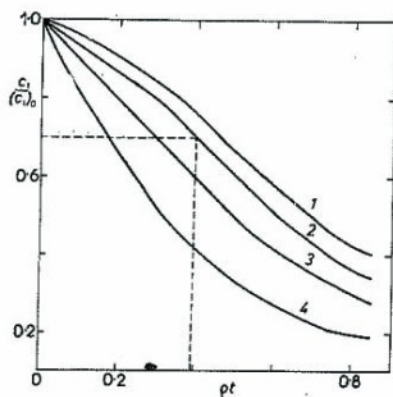


FIG. 2

Dependence of  $c_1/(c_1)_0$  on  $\varrho t$  for chosen parameters  $A$  4 according to Eq. (13). 1  $A = 0.2$ ; 2  $A = 0.3$ ; 3  $A = 0.5$ ; 4  $A = 1.0$

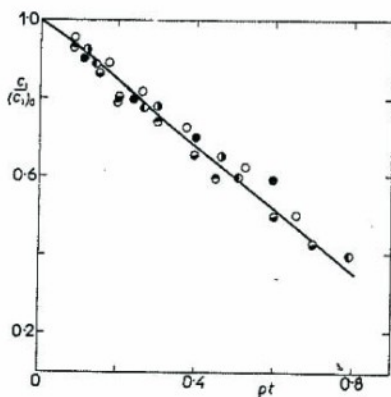


FIG. 3

Comparison of the dependences of  $c_1/(c_1)_0$  on  $\varrho t$  according to Eq. (13) for the determined average value  $A$  0.35 with correlation of experimental data for the determined parameters  $\varrho$  at the initial molar ratio (THF + I): Na : dicyclohexylamine = 26 : 1 : 1 (Table I);  $(c_1)_0$  (in  $\text{mol l}^{-1}$ ): 8.1 ○, 7.3 ●, 5.8 ○, 5.0 ●, 3.3 ○, 1.7 ●

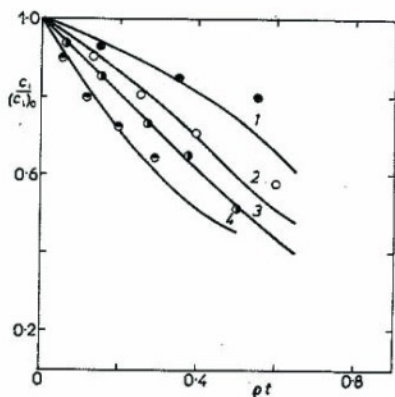


FIG. 4

Comparison of the dependences of  $c_1/(c_1)_0$  on  $\varrho t$  according to Eq. (13) for calculated values of the parameter  $A$  with correlation of experimental data for the determined values of the parameter  $\varrho$  at the initial molar ratio THF : Na : amine 13 : 1 : 1 (Table I). 1  $A = 0.13$ ; 2  $A = 0.34$ ; 3  $A = 0.56$ ; 4  $A = 0.87$

with conditions

$$-C_2 = (1 + A)/(1 - A) \quad (14)$$

$$-2DC_2/k'_1k_2 = 4(c_1)_0/(1 - A)^2, \quad (15)$$

$$\varrho = D^{0.5}/2, \quad (16)$$

where  $\varrho$  and  $A$  are parameters. For parameter  $A$  one can derive, by combining (10), (13) and (9), that

$$A = \{1 - [k'_1k_2(c_1)_0/2\varrho^2]\}^{0.5}, \quad (17)$$

where

$$2\varrho^2 = [k'_1 + k_2(c_Q)_0]^2/2 + k'_1k_2(c_1)_0. \quad (18)$$

Differentiation of Eq. (13) and substitution  $t = 0$  into arguments of hyperbolic functions give for the product of parameters  $\varrho$  and  $A$ :

$$r_0/(c_1)_0 = 2\varrho A. \quad (19)$$

Eq. (19), into which measurable values of the initial isoprene consumption rate,  $r_0$ , and the initial isoprene concentration,  $(c_1)_0$ , can be substituted, was used in the calculation of the parameters  $\varrho$  and  $A$ .

Fig. 2 shows the dependence of the function  $c_1/(c_1)_0$  on  $qt$  for various values of  $A$  and suggests the way of calculation of parameters  $\varrho$  and  $A$ . The value of  $A$  was estimated. For the estimate, the product  $qt$  for  $c_1 = 0.7(c_1)_0$  was ascertained. By dividing the product  $qt$  with the real time at which  $c_1 = 0.7(c_1)_0$  (Fig. 1) was reached, the first estimate of  $\varrho$  was obtained. Substitution of the estimated  $\varrho$  into Eq. (19) along with the respective values of  $r_0$  and  $(c_1)_0$  gave the corrected value of parameter  $A$ . The calculation cycle was repeated until two subsequent values of parameter  $A$  differed by less than (0.01). On the experimental condition that the initial molar ratio (THF + I) : Na : dicyclohexylamine is 26 : 1 : 1 (Table I), the average value of parameter  $A$  lies close to 0.35. According to Eqs (17), (18), it must hold, under the circumstances, that

$$[k'_1 + k_2(c_Q)_0]^2/2 : k'_1k_2(c_1)_0 \doteq 1 : 10 \quad (20)$$

and the magnitude of parameter  $A$  is little sensitive to a change in the isoprene concentration (Fig. 3). Hence, in the subsequent two series of experiments, the conditions were chosen so (Table I) that in one series there was a constant initial molar ratio of isoprene, sodium and dicyclohexylamine (for the investigation of the effect of THF), while in the other series the ratio of THF, Na and amine was constant;



in this case, the ratio of the terms of (20) assumed a limiting value of about 10 : 1, which demonstrates the high dependence of parameter  $A$  on the isoprene concentration (Fig. 4).

By using a simple kinetic reaction model, a very good description of the time dependence of the isoprene concentration was obtained even for high values of the isoprene conversion,  $(c_1/c_1)_0 \approx 0.5$ . The result indicates that a simplifying conception of the reaction mechanism leading to a kinetic model may to a great extent be regarded as adequate.

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Translated by L. Kopecká.

# <sup>29</sup>Si AND <sup>13</sup>C NMR SPECTRA OF SOME ALKYLDIPHENYLCHLOROSILANES, ALKYLDIPHENYLSILANOLS AND BIS(ALKYLDIPHENYLSILYL)CHROMATES

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<sup>29</sup>Si and <sup>13</sup>C NMR spectra of alkyldiphenylchlorosilanes, alkyldiphenylsilanols, and diphenylsilylchromates (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(R)X have been studied. The chemical shifts are most affected by nature of the electronegative substituent X, i.e. Cl, OH or CrO<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. The δ(<sup>29</sup>Si) shifts due to effects of the substituents R can be correlated with values of the Taft constants σ\*. Slopes of the correlation dependences have negative values for all the groups of the studied compounds (increasing electron-acceptor ability of substituents R causes upfield shifts of δ(<sup>29</sup>Si)), and their values decrease with increasing electronegativity of the substituent X (sensitivity of the δ(<sup>29</sup>Si) shifts due to substituent R increases with increasing electronegativity of the substituent X). Methyl groups at γ-position of the chain of substituents R cause a diamagnetic shift of δ(<sup>29</sup>Si) by 0.6 to 3.3 ppm. The δ(<sup>13</sup>C) shifts depend little on the nature of the substituent X. Chemical shifts δ(<sup>13</sup>C) of carbon atoms at α-, β-, and γ-positions of the substituent R with respect to silicon show a good linear correlation with the δ(<sup>13</sup>C) shifts of corresponding carbon atoms in aliphatic hydrocarbons CH<sub>3</sub>R. Slopes of the correlation dependences of all the groups of studied compounds are close to 1, the intercepts for α- and β-positions are negative because of induction effect. Positive value of the intercepts for γ-position is due to the influence of steric γ-effect.

Our previous paper<sup>1</sup> summarizes results of studies of <sup>13</sup>C, <sup>29</sup>Si, <sup>117</sup><sup>119</sup>Sn NMR spectra of the compound type (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>YX, where Y are elements of the IVb group of periodic system (C, Si, Ge, Sn), and X are halogen atoms, hydrogen atom, or CrO<sub>3</sub>OY(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> group. Out of these compounds the most important industrially are esters of chromic acid ((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>YO)<sub>2</sub>CrO<sub>2</sub> which are used as catalysts in catalytic systems for low-pressure polymerization of α-olefins<sup>2,3</sup>.

Besides perphenylsilyl chromates analogous ester with one alkyl instead of phenyl group (i.e. type ((C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(R)O)<sub>2</sub>CrO<sub>2</sub>) have gained technical importance. The present paper deals with a study of <sup>29</sup>Si and <sup>13</sup>C NMR spectra of bis(diphenylsilyl) chromates and compounds of general formulae (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(R)O(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(R)OH, where R = methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, octyl, benzyl, and cyclohexyl. Alkyldiphenylchlorosilanes and alkyldi-