

Synthesis of 2-Methoxy-3-pentene in a Liquid Phase over a Sulfoionite Catalyst: I. Chemical Equilibrium and Reaction Mechanism

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Received September 25, 2000

Abstract—The thermodynamic equilibrium and mechanism of the catalytic synthesis of 2-methoxy-3-pentene from 1,3-pentadiene isomers and methanol are considered. The structures of reaction products were identified by spectroscopic methods, the chemical equilibrium parameters were determined experimentally, and the partial thermodynamic functions were determined by approximation techniques. The mechanism and direction of the main reaction up to the formation of 2-methoxy-3-pentene were substantiated in terms of the most probable intermediates, secondary allyl carbonium ions.

INTRODUCTION

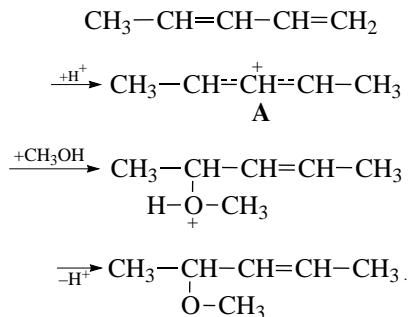
1,3-Pentadiene is a by-product in the dehydrogenation of isopentane to isoprene and in the pyrolysis of hydrocarbon raw materials.

The total quantity of 1,3-pentadiene as piperylene fractions may amount to tens of thousands of tons per year; therefore, its conversion into valuable chemical products is of doubtless interest [1].

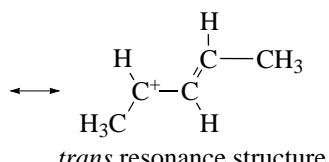
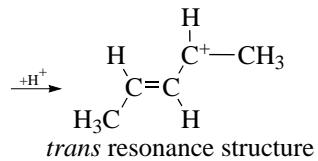
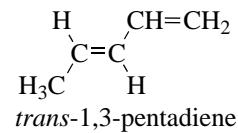
The chromatographic analysis of commercial piperylene fractions showed that the 1,3-pentadiene constituent was a mixture of *trans* and *cis* isomers and the relative concentration of the *cis* isomer ranged from 30 to 45% in the fractions of different origins.

A model mixture of pure *cis* and *trans* isomers of 1,3-pentadiene was examined in the reaction with methanol in the presence of a KIF sulfoionite catalyst [2].

The reaction of methanol with either *cis*- or *trans*-1,3-pentadiene is electrophilic addition catalyzed by a proton of the SO_3H^+ group. It appears to proceed via the formation of allyl carbonium ion (**A**) [3] and gives a single product, *trans*-2-methoxy-3-pentene, by the following mechanism:



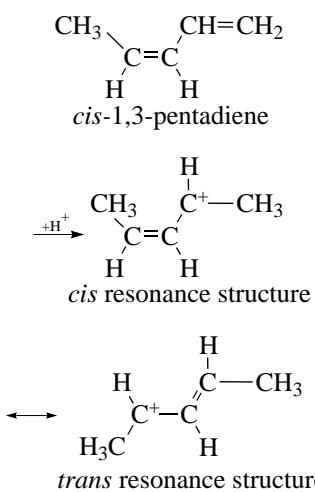
The reaction of *trans*-1,3-pentadiene with methanol in the presence of a sulfoionite catalyst proceeded via the formation of a *trans*-allyl secondary carbonium ion, which, in terms of resonance theory, can be presented as the hybrid of two canonical contributing structures:



The secondary carbonium ion added the nucleophilic agent (methanol) to give the final reaction product *trans*-2-methoxy-3-pentene.

The reaction of *cis*-1,3-pentadiene with methanol in the presence of the above sulfoionite catalyst also pro-

ceeded via the formation of a secondary allyl carbonium ion:



However, in this case, the structure of an intermediate allyl carbonium ion is presented as the hybrid of two different canonical contributing structures (*cis* and *trans*).

It is likely that the *trans* structure, which is also responsible for the formation of *trans*-2-methoxy-3-pentene from *cis*-1,3-pentadiene, made the greatest contribution to the stability of the resulting allyl carbonium ion (**A**).

It is worth noting that allyl carbonium ions formed in the isomerization of ethylene oxides containing a vinyl group in the oxide ring underwent similar isomerization [4].

SUBSTANTIATION OF THE PROPOSED REACTION MECHANISM

The formation of *trans*-2-methoxy-3-pentene from both *cis* and *trans* isomers of 1,3-pentadiene was confirmed by the spectroscopic analysis of the structure of a product resulting from the interaction between the mixture of 1,3-pentadiene isomers and methanol and by the fact that decomposition of *trans*-2-methoxy-3-pentene yielded 1,3-pentadiene that consisted of the *trans* isomer to the extent of 94–95% (the remaining was the *cis* isomer).

trans-2-Methoxy-3-pentene was decomposed in the presence of the same sulfoionite catalyst. The ^1H NMR spectra were measured in CCl_4 using a Tesla BS-467C spectrometer. Chemical shifts were determined with respect to the internal standard hexamethyldisiloxane. The IR spectra were taken using a UR-10 instrument.

The following concentrations of elements were found from the spectroscopic data for *trans*-2-methoxy-3-pentene (%): C, 71.81; O, 15.92; H, 11.27. Calcd. (%): C, 72.00; O, 16.00; H, 12.00 ($\text{C}_6\text{H}_{12}\text{O}$).

A band at 970 cm^{-1} assigned to CH bending vibrations in $-\text{CH}=\text{CH}-$ (*trans*) and a band at 1678 cm^{-1}

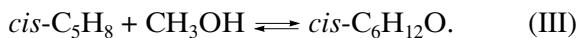
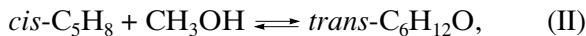
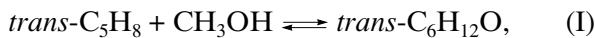
assigned to $-\text{CH}=\text{CH}-$ (*trans*) stretching vibrations were detected in the IR spectrum.

In the ^1H NMR spectrum, a doublet of protons of the methyl group at $\delta = 2.12\text{ ppm}$ ($j = 6.7$; $j_r = 1.5\text{ Hz}$); a signal of the proton at the double bond at $\delta = 6.8\text{ ppm}$ ($j = 15.3$; $j_r = 6.8\text{ Hz}$), which corresponded to the *trans* system; and a signal of protons of the $-\text{O}-\text{CH}_3$ group at $\delta = 3.69\text{ ppm}$ were detected.

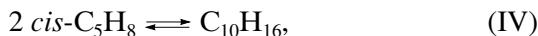
The compositions of 1,3-pentadiene isomer mixtures were determined by chromatography with the use of a thermal-conductivity detector and PEG 1500 and PEG 3000 as stationary phases.

THERMODYNAMIC EQUILIBRIUM IN THE REACTIONS OF 2-METHOXY-3-PENTENE SYNTHESIS

It appears that several parallel reactions may occur during the interaction between 1,3-pentadiene and methanol which can be represented as follows:



1,3-Pentadiene can form dimers, and the formation of dimethyl ether from methanol is also possible:



Because reactions (IV), (V), and (VI) proceeded to a negligible extent under real conditions, no consideration has been given to them.

Partial thermodynamic quantities for the ethers formed in reactions (I)–(III) have not been published, and we determined them by approximation techniques (the Franklin, Anderson–Beyer–Watson, and Van Krevelen methods [5]).

The calculated values of ΔH_{298}^0 and ΔG_{298}^0 for the formation of ethers are presented in Table 1.

The Gibbs energies and enthalpies for the liquid state were obtained by known relationships.

The heats of ether vapor condensation H_v^T were calculated by the Vvedenskii and Watson methods [6]. The H_v^T values obtained at the boiling point were 32.94 and 31.94 kJ/mol, respectively. In further calculations, we chose the H_v^T value obtained by the Vvedenskii equation, which was more reliable because we used our experimental relationships between temperature and vapor pressure of 2-methoxy-3-pentene in these calculations (Table 3).

Thermodynamic constants of the chemical equilibrium at 25°C were calculated from the equation of the

Table 1. Gibbs energies and enthalpies of reactions between 1,3-pentadienes and methanol calculated by the Franklin*, Anderson–Beyer–Watson**, and Van Krevelen*** methods

Reaction	ΔH_{298}^0 , kJ/mol		ΔG_{298}^0 , kJ/mol	
	gas	liquid	gas	liquid
(I)	−47.48*	−16.25	−8.50**	−9.38
(II)	−47.90*	−16.29	−7.70**	−8.37
(III)	−43.50*	−11.89	−4.69**	−5.40
(I)	−42.79**	−11.56	13.15***	12.27
(II)	−43.21**	−11.60	13.94***	13.27
(III)	−39.44**	−7.83	16.58***	15.91

Table 2. Experimental data on the thermodynamic equilibrium of the synthesis of *trans*-2-methoxy-3-pentene in a liquid phase

T, °C	Initial molar ratio between methanol and 1,3-pentadienes	Composition of the equilibrium mixture, mol %					Equilibrium constant K_{eq} in terms of concentration
		total 1,3-pentadienes	methanol	<i>trans</i> -2-methoxy-3-pentene	1,3-pentadiene dimers	conversion of total 1,3-pentadienes to the ether, %	
50	0.29	71.85	1.54	26.61	—	27.00	24.05
	1.23	19.75	34.93	45.32	—	69.80	6.57
	1.99	10.20	54.78	35.02	—	77.60	6.28
	3.48	5.63	72.86	21.51	—	79.30	5.24
70	0.28	70.09	2.10	25.03	2.78	24.50	17.01
	1.25	23.65	38.92	37.43	—	61.30	4.06
	2.93	8.92	69.01	22.07	—	71.20	3.58
	3.86	6.28	75.71	18.01	—	74.20	3.79
90	0.23	65.31	2.18	19.97	12.53	18.00	4.03
	0.32	58.27	4.28	26.20	11.25	23.30	10.50
	0.99	32.53	32.02	34.97	0.47	50.90	3.36
	3.92	7.81	76.56	15.46	0.17	65.40	2.59

chemical reaction isotherm and, at higher temperatures, from the van't Hoff reaction isobar.

Additive group methods used in the calculations of heats of formation and Gibbs energies were, as a rule, accurate to ± 20 kJ/mol [5].

It follows from Table 1 that all main reactions were exothermal. The greatest difference in Gibbs energies calculated for these reactions by different methods was more than 20 kJ/mol. Because an error of ~ 4 kJ/mol in the determination of ΔG_{298}^0 changed the true value of

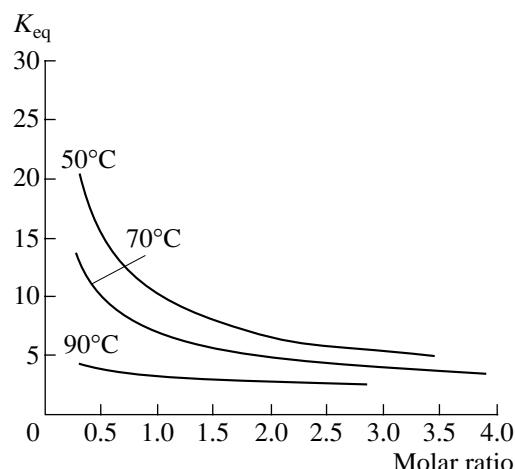


Fig. 1. Equilibrium constant K_{eq} in terms of concentration as a function of the initial molar ratio between reactants at different temperatures.

K_{eq} by a factor of $\sim e^{500/T}$, the experimental study of the chemical equilibrium in the test system was necessary.

EXPERIMENTAL DATA

The thermodynamic equilibrium was studied in model mixtures in the presence of a KIF sulfoionite catalyst.

trans-1,3-Pentadiene was obtained by decomposing *trans*-2-methoxy-3-pentene over the sulfoionite catalyst. 1,3-Pentadiene, which was washed from methanol and dried over aluminum oxide, contained $\sim 97\%$ *trans*-1,3-pentadiene and the balance was *cis* isomer.

cis-1,3-Pentadiene was isolated from a mixture of the isomers by binding *trans*-1,3-pentadiene with maleic anhydride to a high-boiling adduct followed by separating the *cis* isomer by rectification. To shorten the equilibration time, we used model mixtures that were

close to calculated equilibrium mixtures in composition. The attainment of the thermodynamic equilibrium in the system was judged from the constancy of composition of the equilibrium mixture to within the error of the chromatographic analysis.

Thermodynamic equilibrium was studied using a glass tube provided with a temperature-controlled jacket and samplers. The apparatus was placed in a metal case fixed on a shaker with a speed of ~ 40 oscillations per minute. Because both of the 1,3-pentadiene isomers formed the same *trans*-ether, in our further thermodynamic studies, we conventionally considered the initial mixture of isomeric 1,3-pentadienes as a single substance, 1,3-pentadiene, and the product of interaction between geometrical isomers of 1,3-pentadiene and methanol, as a single product, *trans*-2-methoxy-3-pentene.

The experimental data on the thermodynamic equilibrium in the synthesis of *trans*-2-methoxy-3-pentene are summarized in Table 2.

It follows from Table 2 that experimental equilibrium constants K_{eq} on a concentration basis are functions of the concentrations of components in the initial mixture.

Equilibrium constants were calculated from the equation

$$K_{\text{eq}} = \frac{X_e}{X_{\text{pd}} X_m}, \quad (1)$$

where X_e , X_{pd} , and X_m are the concentrations of the ether, pentadienes, and methanol expressed in mole fractions, respectively.

The accuracy of calculating K_{eq} was governed by the accuracy of the chromatographic analysis of equilibrium compositions of the products of *trans*-2-methoxy-3-pentene synthesis and equaled $\pm 5\text{--}10$ rel %.

It is known that the mixtures of hydrocarbons and ethers with methanol are characterized by a significant

Table 3. Constants of the Antoine equation for the determination of the saturation vapor pressure of substances (the equation is applicable in the temperature range from -60 to $+120^\circ\text{C}$; accuracy class 1 [7]; the error in the determination of *trans*-2-methoxy-3-pentene vapor pressure was $< 0.05\%$)

Substance	Antoine constants			References
	A	B	C	
<i>trans</i> -1,3-Pentadiene	6.92257	1108.94	232.34	[1]
<i>cis</i> -1,3-Pentadiene	6.94179	1118.37	231.33	[1]
Methanol	7.88597	1475.145	230.00	[6]
<i>trans</i> -2-Methoxy-3-pentene	6.9554	1271.957	222.2477	Our experimental data

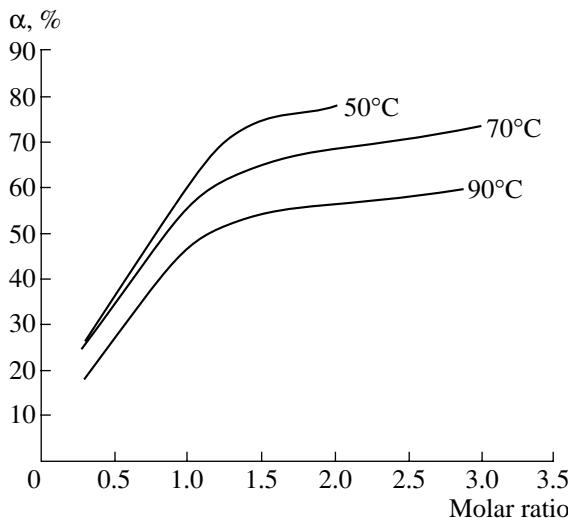


Fig. 2. Equilibrium conversion of 1,3-pentadiene to *trans*-2-methoxy-3-pentene as a function of the initial molar ratio between reactants at different temperatures.

deviation in the behavior of components from ideality. Taking this into account, one can assume that the neglect of activity coefficients was the reason for a change in the equilibrium constant.

Figure 1 presents the equilibrium constant K_{eq} in terms of concentration as an approximated function of the initial molar ratio between reactants. It can be seen in Fig. 1 that the equilibrium constant changed as the initial molar ratio between reactants varied from 0.3 to 1.5, especially in the temperature range 50–70°C. At initial molar ratios higher than 1.5–2.0, the equilibrium constant only slightly changed under isothermal conditions.

To account for the nonideality of the liquid phase, we calculated the activity coefficients for components using the Wilson equation [5] in the form

$$\ln \gamma_k = -\ln \left[\sum_j x_j \Lambda_{kj} \right] + 1 - \sum_i \frac{x_i \Lambda_{ik}}{\sum_j x_j \Lambda_{ij}}, \quad (2)$$

where Λ_{kj} , Λ_{ik} , and Λ_{ij} are the numerical parameters that take into account differences in the intermolecular “attraction” of components.

The equilibrium constants K_a , calculated with activity coefficients taken into account, are presented in Table 4. The average values of the equilibrium constants K_a in terms of activity were 2.83, 1.99, and 1.43 at 50, 70, and 90°C, respectively.

As the temperature increased, the equilibrium constant decreased; such behavior is characteristic of exothermal reactions.

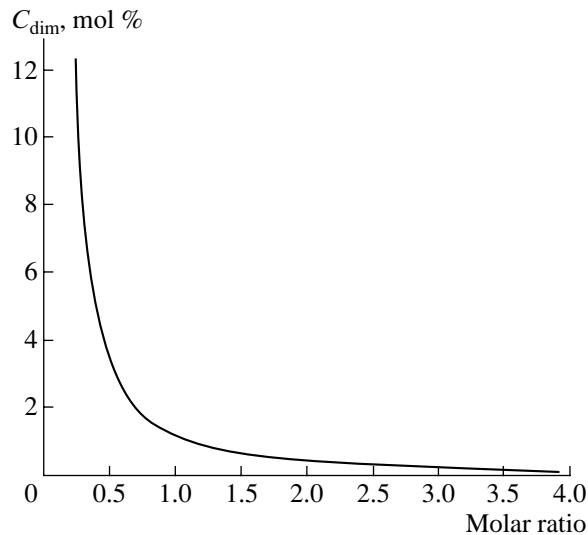


Fig. 3. Concentration of 1,3-pentadiene dimers in the reaction mixture as a function of the initial molar ratio between reactants at 90°C.

The enthalpy ΔH of the synthesis of 2-methoxy-3-pentene calculated from the values of K_a found at different temperatures was equal to 16.70 kJ/mol.

Figure 2 presents the equilibrium conversion of 1,3-pentadiene to the *trans* ether (α) as a function of the initial molar ratio between methanol and 1,3-pentadiene at different temperatures. A significant growth in the conversion of 1,3-pentadiene with an increase in initial molar ratios of components up to ~2 is evident. It is likely that this was due to the corresponding shift of the reaction equilibrium. When 1,3-pentadiene was taken in excess, an increase in the concentration C_{dim} of dimerization products was observed (Fig. 3). A temperature of 70–80°C and an initial molar ratio between reactants of 1.5–2.0 appeared to be optimal conditions for *trans*-2-methoxy-3-pentene synthesis. The activity coefficients of components calculated from equilibrium compositions given in Table 2 are presented in Table 4. The values of K_a were calculated by the equation

$$K_{\text{eq}} = \frac{a_e}{a_{\text{pd}} a_m}, \quad (3)$$

where a_e , a_{pd} , and a_m are the activities of the ether, 1,3-pentadiene, and methanol, respectively. The activity of a component was determined as the product of the component concentration in solution by γ .

Thus, 1,3-pentadiene reacted with methanol in the presence of the sulfoionite catalyst to form *trans*-2-methoxy-3-pentene. This was due to the *cis*–*trans* isomerization of the intermediate, secondary allyl carbonium cation. In the decomposition of *trans*-2-methoxy-3-pentene, *trans*-1,3-pentadiene was formed.

Table 4. Experimental equilibrium constants in terms of activity for *trans*-2-methoxy-3-pentene synthesis in a liquid phase

T, °C	Number of runs	Molar ratio between methanol and 1,3-pentadienes	γ for <i>trans</i> -2-methoxy-3-pentene	γ _{methanol}	γ _{1,3-pentadiene}	K _γ	K _a	Relative error in the determination of K _a , %
50	3	0.29	1.00	9.39	1.01	0.11	2.53	10.90
	3	1.23	1.16	1.87	1.51	0.41	2.69	5.28
	2	1.99	1.48	1.34	2.14	0.52	3.22	13.38
	2	3.48	2.00	1.12	3.21	0.56	2.91	2.46
70	3	0.28	1.00	8.82	1.01	0.11	1.90	4.52
	2	1.25	1.20	1.75	1.56	0.44	1.78	10.55
	2	2.93	1.85	1.16	2.78	0.57	2.06	3.52
	3	3.86	2.11	1.09	3.30	0.59	2.21	11.06
90	2	0.23	1.00	9.55	1.01	0.10	1.45	0.69
	2	0.32	1.00	7.31	1.02	0.13	1.38	4.17
	4	0.99	1.12	2.05	1.39	0.39	1.33	7.64
	2	3.92	2.14	1.09	3.21	0.61	1.58	9.72

Note: The error in the determination of γ was $\pm 5\%$, and those in the determination of K_γ and K_a were $\pm 15\%$.

A high yield of the ether makes it possible to accomplish the reaction on a commercial scale.

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