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Molar enthalpies of formation and vaporization of *t*-butoxybutanes and thermodynamics of their synthesis from a butanol and 2-methylpropene I. Equilibria of synthesis reactions of *t*-butoxybutanes in the liquid phase

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The equilibria of the synthesis of 1-*t*-butoxybutane [I], 2-methyl-1-*t*-butoxypropane (II), and 1-methyl-1-*t*-butoxypropane (III) from 2-methylpropene (IV), and butan-1-ol (V), 2-methylpropan-1-ol (VI), and butan-2-ol (VII) in the liquid phase were investigated at temperatures from 315 K to 423 K. On the basis of experimental equilibrium constants found for $n(C_4H_9OH)/n\{(CH_3)_2C:CH_2\} = 4$, values of $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$ were calculated. The following results were obtained:

Reaction	$\Delta_{\rm r} H_{\rm m}^{\circ}/({\rm kJ}\cdot{\rm mol}^{-1})$	$\Delta_r S^{\circ}_m/(\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1})$
V + IV = I	-34.8 ± 2.7	-75.8 ± 7.7
VI + IV = II	-36.3 ± 1.8	-79.6 ± 5.2
VII + IV = III	-37.7 ± 2.4	-108.5 ± 7.3

1. Introduction

t-Butoxyalkanes are used in industry as high-octane additives to motor fuels which do not contain tetraethyl lead. This reason stimulated the development of investigations about synthesis and studies of the properties of these compounds.

The basic method to prepare *t*-butoxyalkanes includes interaction of the corresponding alkanol with 2-methylpropene in the presence of a catalyst. This is an equilibrium reaction and, hence, investigations of the thermodynamics of synthesis processes are needed.

The values given in the literature on the thermodynamics of the synthesis of ethers

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from alcohols and isoolefins are very limited. They deal mostly with processes of synthesis of 2-methyl-2-methoxypropane⁽¹⁻⁴⁾ and 2-ethyl-2-methoxypropane.^(5,6) As for the ethers of higher alcohols, the information about them is limited. At present, our laboratory is conducting systematic investigations of the thermodynamics of the synthesis processes of ethers on the basis of alcohols C₁ to C₅ in the liquid and gas phases. The results have been given previously.^(4, 6-9) To continue these investigations, we studied the equilibria of liquid-phase reactions of 2-methylpropene with butan-1-ol, 2-methylpropan-1-ol, and butan-2-ol and found enthalpies of vaporization and combustion of 1-t-butoxybutane, 2-methyl-1-t-butoxypropane, and 1-methyl-1-t-buroxypropane. This paper shows the results of the investigation of the equilibria of the reactions of the synthesis of the results of the synthesis of the synthesis of the reactions of the synthesis of the results of the synthesis of th

2. Experimental

Equilibria of the reactions:

$$C_4H_9OH + CH_2:C(CH_3)_2 = C_4H_9 - O - C(CH_3)_3,$$
 (1)

$$CH_{3}CH(CH_{3})CH_{2}OH + CH_{2}:C(CH_{3})_{2} = CH_{3}CH(CH_{3})CH_{2} - O - C(CH_{3})_{3}, \quad (2)$$

$$CH_{3}CH(OH)CH_{2}CH_{3} + CH_{2}:C(CH_{3})_{2} = CH_{3}CH_{2}CH(CH_{3}) - O - C(CH_{3})_{3}, \quad (3)$$

were investigated in the liquid phase in sealed glass ampoules in the presence of sulfocationite KU-23 as a catalyst at temperatures from 315 K to 423 K.

As was shown elsewhere,⁽⁹⁾ and taking the investigation of the equilibria of 1-*t*-butoxypentane synthesis as an example, the mole-fraction equilibrium products K_x became stable at $n(C_5H_{11}OH)/n\{(CH_3)_2C:CH_2\} \ge 3$ in the starting mixture. (Butanol + 2-methylpropene + *t*-butoxybutane) behaves analogously. This was found for all butanols on the basis of special experiments made at 323 K and with $n(C_4H_9OH)/n\{(CH_3)_2C:CH_2\}$ from 1 to 8. On the basis of the results obtained as well as the values from our earlier work,⁽⁹⁾ the investigation of equilibrium was made with $n(C_4H_9OH)/n\{(CH_3)_2C:CH_2\} = 4$. The criteria for equilibrium were the stability of the equilibrium constant on changing the starting product (direct or reverse reaction), quantity of the catalyst, and time of the reaction.

Commercial 2-methylpropene (99.8 mass per cent), butan-1-ol (99.9 mass per cent), 2-methylpropan-1-ol (99.9 mass per cent), and butan-2-ol (99.8 mass per cent) were used for the investigation. t-Butoxybutanes were prepared in the laboratory through interaction of 2-methylpropene with the corresponding alkanol and purified by distillation. They had (99.0 to 99.5) mass per cent purities. The analysis of the reaction products was made by g.l.c. with the help of a "Chrom-4" apparatus with a flame-ionization detector on a packed column 2.5 m long, filled with 5 mass per cent of SE-30 on AW-HMDS Inertone. The column temperature was 353 K and the evaporator temperature was 453 K. Helium was used as a carrier gas. The results of the experiments are shown in table 1.

value of the mole-fraction equilibrium products K_x						
N ^a	x(C ₄ H ₉ OH)	x(ether)	$x\{(CH_3)_2C:CH_2\}$	$\langle K \rangle$		
	Reaction 1					
6 (7)	0.7533	0.2336	0.01316	23.56 ± 1.05		
5 (5)	0.7556	0.2220	0.02244	13.10 ± 0.44		
5 (5)	0.7595	0.2023	0.03820	6.97 ± 0.34		
7 (7)	0.7659	0.1703	0.06374	3.49 ± 0.26		

0.07285

0.01360

0.02439

0.04251

0.06459

0.08946

0.05993

0.07692

0.09147

0.1145

0.1321

0.1492

0.1589

0.2330

0.2195

0.1968

0.1693

0.1382

0.1751

0.1538

0.1357

0.1069

0.08481

0.06344

TABLE 1. Results for reactions (1) to (3) in the liquid phase in the presence of sulfocationite KU-23; w, mass fraction of catalyst; τ , time of the experiment; N, number of experiments; x, mole fraction in equilibrium mixture; $\langle K \rangle$, mean value of the mole-fraction equilibrium products K_x

0.7682

Reaction 2

0.7534

0.7561

0.7606

0.7661

0.7724

Reaction 3

0.7650

0.7692

0.7729

0.7786

0.7830

0.7873

" For reaction or, in parentheses, the reverse of the reaction.

T/K

341

358 378

403

413

343

363

383

403

423

315

324 331

343

353

364

 $10^2 \cdot w$

10 to 15

10 to 15

10 to 12

8 to 10

8 to 10

10 to 15

10 to 15

10 to 12

8 to 10

8 to 10

10 to 15

10 to 15

10 to 15

10 to 15

8 to 15

8 to 15

τ/h

2 to 10

1.5 to 6

1.5 to 3

0.5 to 2

0.5 to 2

9 to 23

9 to 15

10 to 17

8 to 16

3 to 8

5 to 14

2 to 4.5

1.5 to 8

1.5 to 3

1.5 to 5

0.75 to 2

7 (7)

6 (7)

7 (7)

7 (5)

6 (6)

7 (6)

6 (6)

6 (6)

6 (6)

6 (6)

6 (6)

6 (6)

3. Results and discussion

Relations of the mole-fraction equilibrium products with temperature were found by the method of least squares with the experimental values shown in table 1:

$$\lg K_x = a + b(K/T). \tag{4}$$

Values of $\Delta_r H_m^{\circ}$ and $\Delta_r S_m^{\circ}$ of reactions (1) to (3) were calculated. The results are shown in table 2.

Our earlier paper⁽⁹⁾ showed (taking as an example the reaction of synthesis of 1-t-butoxypentane) that in liquid non-ideal (alkanol + 2-methylpropene + ether)

TABLE 2. Values of $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$ and coefficients of the equation $\lg K_x = a + b(K/T)$ for reactions (1) to (3) in the liquid phase

Reaction	- <i>a</i>	b	$\frac{\langle T \rangle}{K}$	$\frac{-\Delta_{\rm r}H_{\rm m}^{\circ}}{\rm kJ\cdot mol^{-1}}$	$\frac{-\Delta_{\mathbf{r}}S_{\mathbf{m}}^{\circ}}{\mathbf{J}\cdot\mathbf{K}^{-1}\cdot\mathbf{mol}^{-1}}$
1	3.96	1818	377.0	34.8+2.7	75.8 ± 7.7
2	4.16	1894	383.0	36.3 ± 1.8	79.6 ± 5.2
3	5.67	1971	339.5	37.7±2.4	108.5 ± 7.3

 2.84 ± 0.27

22.77 + 0.36

 11.90 ± 0.31

 6.09 ± 0.18

 3.42 ± 0.21

 2.00 ± 0.13

 3.82 ± 0.10

 2.60 ± 0.09

 1.92 ± 0.05

 1.20 ± 0.07

 0.82 ± 0.04

 0.54 ± 0.04

the value of $K_{\gamma} = \gamma_{\text{ether}} \cdot \gamma_{alkanol}^{-1} \cdot \gamma_{2\text{-methylpropene}}^{-1}$ (where γ is the activity coefficient) which characterizes the deviation of the system from ideality, does not depend on the composition of the equilibrium mixture when the reaction is conducted with excess alkanol. That means that $\Delta_r H_m^\circ$ calculated from the mole-fraction equilibrium products found at $n(C_4H_9OH)/n\{(CH_3)_2C:CH_2\} \ge 3$ corresponds to the true value of the enthalpy of reaction. Values of $\Delta_r S_m^\circ$ found through the relation of the mole-fraction equilibrium products differ from the true values by $R \cdot \ln K_{\gamma}$. The experimental values of $\Delta_r H_m^\circ$ will be dealt with after the above conditions have been taken into account.

According to the results⁽¹⁰⁾ for the analogous gas-phase reactions of the synthesis of 2-methyl-2-methoxypropane from methanol and 2-methylpropene and of ethoxyethane from ethanol and ethene, the value of $\Delta C_{p,m}$ is insignificant (about $3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). With due account taken of these conditions and a low value of the average temperature of the experiment (about 380 K), the experimental values of $\Delta_r H_m^\circ$ can be taken to refer to 298.15 K. With great probability it can be suggested that $\Delta_r H_m^\circ$ s of reactions (1) and (2) are equal, as a primary alkanol reacts in both cases. The values of the mole-fraction equilibrium products should also be close to the above. The latter assumption is based on the results obtained by us earlier on the dependence of the mole-fraction equilibrium products for the reaction of synthesis of the ethers from a normal alkanol and 2-methylpropene at 323 K and stoichiometric correspondence of the reacting components.⁽⁸⁾ According to the results, the mole fractions of the equilibrium products change little in the transition from 1-t-butoxypropane to 1-t-butoxypentane. This is supported by the results of the present paper. Thus, at 403 K, the values of K_x of reactions (1) and (2) are 3.49 and 3.42, respectively. Values of $\Delta_r H_m^\circ$ of these reactions do not differ noticeably.

As for the results of reaction (3), noticeable differences are seen from the results of the first reactions. First of all, the values of the mole-fraction equilibrium products are approximately 20 times smaller than for reactions (1) and (2). Such a change in K_x is connected mainly with the entropy. It is impossible to state definitely why there are such distinct differences in $\Delta_r S_m^\circ$ of those reactions. The answer may possibly be found with the accumulation of experimental values on analogous systems.

The value of $\Delta_r H_m^\circ$ of reaction (3), $-37.7 \text{ kJ} \cdot \text{mol}^{-1}$, is slightly different from the values of $-34.8 \text{ kJ} \cdot \text{mol}^{-1}$ and $-36.3 \text{ kJ} \cdot \text{mol}^{-1}$, though it is difficult to say whether the difference is connected with the difference in the strength of the bond of a secondary carbon atom with oxygen or an error in measurement. Analysis of the differences between $\Delta_r H_m^\circ$ of propan-1-ol and 1-methoxypropane and of propan-2-ol and 2-methoxypropane shows, according to the values from reference 11, that the difference: $\Delta\Delta_r H_m^\circ = \{\Delta_r H_m(\text{ether}) - \Delta_r H_m(\text{alkanol})\}$, is practically constant (38.6 kJ · mol⁻¹ and 39.3 kJ · mol⁻¹).

Comparison of the experimental values of $\Delta_r H_m^{\circ}$ for reactions (1) to (3) with the available literature values shows good agreement. Thus, for the reaction of pentan-1-ol with 2-methylpropene,⁽⁹⁾ $\Delta_r H_m^{\circ} = -35.66 \text{ kJ} \cdot \text{mol}^{-1}$, which practically coincides with the results of the present paper. The values of the enthalpies of the reactions obtained by us are close to the value of $-39.8 \text{ kJ} \cdot \text{mol}^{-1}$ found⁽¹²⁾ calorimetrically for the synthesis reaction of 2-methyl-2-methoxypropane.

The results of calorimetric measurements of the enthalpy of vaporization and combustion, and the $\Delta_f H_m^{\circ}$ s of ethers will be given in Part II of the present series.

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