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Thermochemistry of Benzyl Alcohol: Reaction Equilibria Involving Benzyl Alcohol and *tert*-Alkyl Ethers

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Chemical equilibrium of the reactive systems of benzyl alcohol with *tert*-alkyl ethers was studied in the liquid phase in the temperature range (298 to 373) K and with a cation exchanger Amberlist 15 as a catalyst. Enthalpies of reactions involving benzyl alcohol were obtained from the temperature dependence of the equilibrium constants according to the *Second Law* and used to derive averaged standard enthalpies of formation of benzyl alcohol $\Delta_f H^\circ_{m(l,298.15K)} = -(154.5 \pm 1.7)\ \text{kJ·mol}^{-1}$ in the liquid state. Vapor pressures and enthalpy of vaporization, $\Delta_l^g H_{m(298.15\ K)}$, of benzyl alcohol were determined using transpiration method. The latter value, together with the reliable literature data, provided an averaged result $\Delta_l^g H_{m(298.15\ K)} = (65.75 \pm 0.51)\ \text{kJ·mol}^{-1}$. Both averaged results for $\Delta_f H^\circ_{m(l,298.15K)}$ and $\Delta_l^g H_{m(298.15\ K)}$ were used to calculate and to recommend the value of enthalpy of formation of benzyl alcohol in the gaseous state $\Delta_f H^\circ_{m(g,298.15K)} = -(88.8 \pm 1.8)\ \text{kJ·mol}^{-1}$. Auxiliary data for *tert*-butyl benzyl ether (energy of combustion, vapor pressures, and enthalpy of vaporization) were measured using calorimetry and transpiration method.

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1. Introduction

The presence of two OH bands in the IR spectra of aliphatic alcohols has been convincingly explained as due to several conformers in the solution.[1] In molecules containing double-bond systems, such as benzyl alcohol, the low-frequency band is ca. 10 cm^{-1} below the corresponding band in the purely aliphatic alcohols. This has led several authors to propose the existence of weak intramolecular hydrogen bonds, the low-frequency band resulting from the bonded conformer.[2,3] Quantification of weak intramolecular hydrogen bonds is difficult because their strength is usually only several kJ per mol. For instance, according to ab initio calculations,[4] the strength of intramolecular hydrogen bonds in benzyl alcohol is only about 4 kJ·mol^{-1}. Thermochemical properties of a molecule, such as enthalpy of formation or enthalpy of vaporization, are very important for the quantification of the hydrogen bond strength,[5] provided that these thermodynamic properties are of high accuracy. Unfortunately, it is not the case for benzyl alcohol. The determination of the $\Delta_f H^\circ_{m(l)}$ of benzyl alcohol has long been a popular endeavor by using combustion calorimetry. The impressive scatter of the experimental values: −(154.9 ± 3.0) kJ·mol^{-1} by Papina et al.[6] from 1995, −(161.0 ± 1.3) kJ·mol^{-1} by Parks et al.[7] from 1954, −174.0 kJ·mol^{-1} by Landrieu et al.,[8] from 1929, and −167.0 kJ·mol^{-1} by Schmidlin[9] from 1906, could be explained by hygroscopic nature of this compound. The more recent work of Papina et al.[6] has been done very carefully; however, its experimental uncertainty is too large, and this fact makes us reticent to involve this result into interpretation of the hydrogen bond strength. Our recent work[10] has confirmed in general the magnitude of the enthalpy of formation of benzyl alcohol, measured by Papina et al.[6] This paper extends our previous studies on the systematic investigation of a series of equilibrium reactions involving branched ethers and has been conducted in order to ascertain the thermochemochemical quantities of benzyl alcohol. In our previous works[11−16] we developed a procedure to determine enthalpies $\Delta_r H^\circ_m$ of etherification reactions from experimental equilibrium constants. The same procedure is applied now in this work to obtain thermodynamic functions of some tert-alkyl ethers (see Figure 1) synthesis reactions (see Figure 2) in the liquid phase, which have been used together with the results from vapor pressure measurements to derive reliable enthalpies of formation of benzyl alcohol in the liquid as well as in the gaseous state.

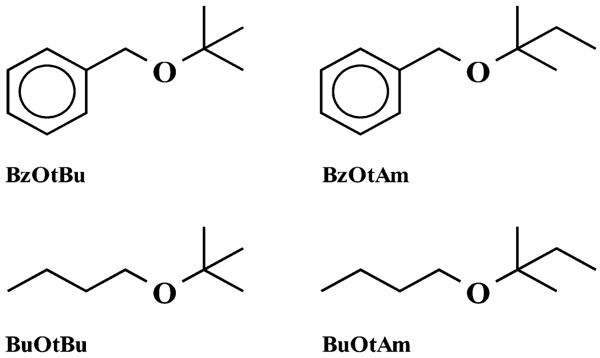

Figure 1. Structures of *tert*-alkyl ethers, involved in the investigation of chemical equilibrium: *tert*-butyl benzyl ether (BzOtBu); *tert*-amyl benzyl ether (BzOtAm); *tert*-butyl butyl ethers (BuOtBu); *tert*-amyl butyl ether (BuOtAm).

2. Experimental Section

2.1. Materials. Benzyl alcohol (BzOH) [100-51-6] and butan-1-ol (BuOH) [71-36-3] were of commercial origin. A technical fraction of isoamylenes (methylbutenes) with the mass percentages of hydrocarbons C_4 1.9; 2-methylbut-1-ene (2MB1) [563-46-2] 39.6; 2-methylbut-2-ene (2MB2) [513-35-9] 56.0; and 3-methylbut-1-ene (3MB1) [563−45−1] 2.5 were used in the experiments. The structures of the branched ethers studied in this work are presented in Figure 1. *tert*-Butyl benzyl ether (BzOtBu) [3459-80-1], *tert*-

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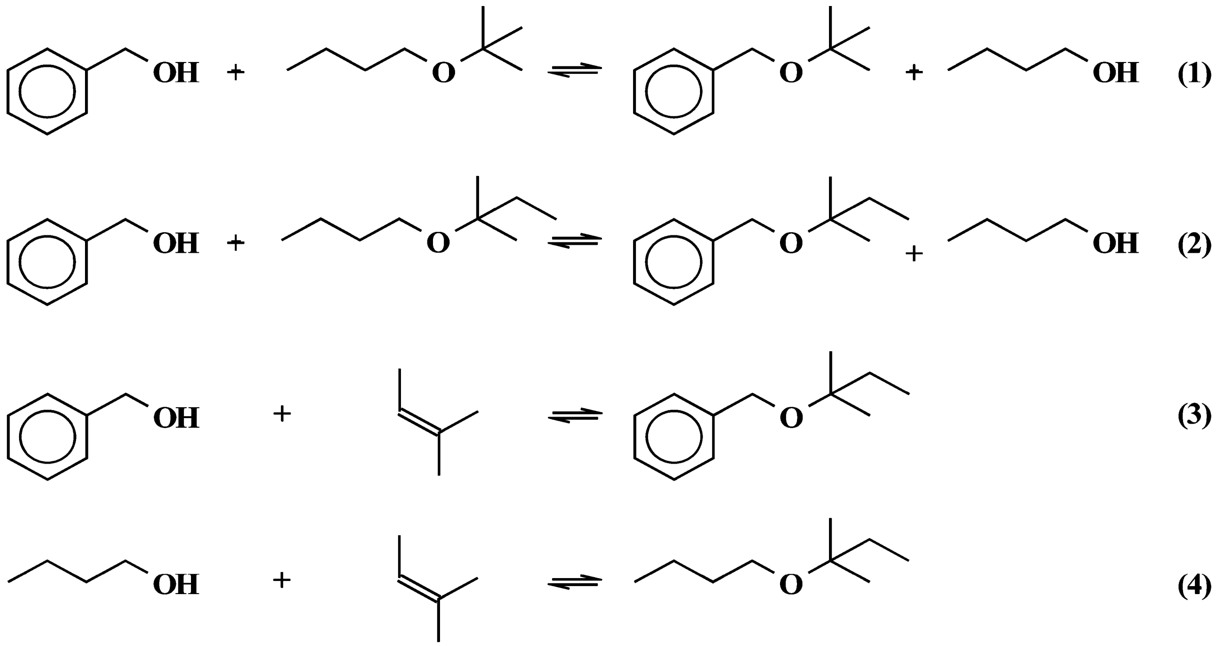

Figure 2. Equilibrium reactions of *tert*-alkyl ethers synthesis studied in this work.

amyl benzyl ether (BzOtAm) [27674-74-4], *tert*-butyl butyl ethers (BuOtBu) [1000-63-1], and *tert*-amyl butyl ether (BuOtAm) [3249-47-6] were synthesized via alkylation of an appropriate alkanol with the olefins in the presence of a catalytic amount of cation-exchange resin in the H^+ form (Amberlist 15, Aldrich) at 343 K. Prior to the experiments, the catalyst was dried for 8 h at 383 K in a vacuum oven at reduced pressure. Pure samples (99.9 mass % determined by gas chromatography (GC)) of branched ethers (Figure 1) were obtained by repeated distillations at reduced pressure, and their structures were confirmed by NMR analysis.

2.2. Chemical Equilibrium Study in the Liquid Phase. Glass vials with screwed caps were filled two-thirds full with the initial liquid mixture of benzyl alcohol and butyl *tert*-alkyl ether or benzyl alcohol and isoamylenes. Cation-exchange resin Amberlist 15 was added as a solid catalyst. The quantity of the catalyst was approximately 10% of the mass of the mixture. The vial was thermostated (with uncertainty 0.1 K) and periodically shaken. After definite time intervals, the vial was cooled rapidly in ice and opened. A sample for the GC analysis was taken from the liquid phase using a syringe. The thermostating of the vial was then continued at the same temperature. The samples were taken successively until no further change of the compositions was observed, indicating that the chemical equilibrium was established. The compositions of the reaction mixtures were determined chromatographically with a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector. A capillary column HP-5 (stationary phase cross linked 5% PH ME silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm. Response factors of all reagents were determined using calibration mixtures of the corresponding components prepared gravimetrically. Accuracy of the GC analysis of the liquid-phase composition was estimated to be within ±0.0005 mass %. The equilibrium ratios Q_x of reactions 1 and 2 were calculated with help of mole fractions x_i of reaction participants

$$Q_x = x_{(\mathrm{BzOtAlk})}x_{(\mathrm{BuOH})}/x_{(\mathrm{BzOH})}x_{(\mathrm{BuOtAlk})} \qquad (5)$$

Table 1. Results from the Liquid-Phase Investigation of Equilibrium of Reaction 1 and Experimentally Determined Composition of Equilibrium Mixtures and Q_x Values in the Liquid Phase, Calculated from Eq 5[a]

T/K	n	x_{BzOH}	x_{BuOH}	x_{BuOtBu}	X_{BzOtBu}	$Q_x(1)$
301.9	7	0.1711	0.3319	0.2450	0.2521	2.00
312.7	8	0.2558	0.3416	0.1744	0.2282	1.75
323.8	2	0.1762	0.5152	0.2053	0.1063	1.51
331.1	4	0.1104	0.7245	0.1358	0.0293	1.42
	7	0.1605	0.5360	0.2116	0.0920	1.45
	5	0.1858	0.5061	0.2032	0.1049	1.41
338.3	4	0.1082	0.6883	0.1695	0.0340	1.28
348.1	3	0.1692	0.6320	0.1557	0.0491	1.18
351.7	4	0.1169	0.7114	0.1434	0.0284	1.21
	6	0.1261	0.5505	0.2605	0.0629	1.05
359.0	4	0.0999	0.5059	0.3247	0.0695	1.08
363.0	4	0.1480	0.5814	0.2141	0.0565	1.04
	6	0.1884	0.6362	0.1345	0.0409	1.03

[a] T is the temperature of investigation, n is number of determinations of composition within the time of equilibrium study, and x_i is the mole fraction determined chromatographically.

The equilibrium ratios Q_x of reactions 3 and 4 were calculated with the help of mole fractions x_i of the reaction participants

$$Q_x = x_{(\mathrm{ether})}/x_{(\mathrm{ROH})}x_{(\mathrm{2MB2})} \qquad (6)$$

Mole fractions at equilibrium x_i and the equilibrium ratios Q_x in the liquid phase are listed in Tables 1 and 2. Response factors of all reagents were determined using calibration mixtures of the corresponding components prepared gravimetrically.

2.3. Combustion Calorimetry. The pure sample of *tert*-butyl benzyl ether was obtained by repeated distillation under N_2 using a spinning-band column at reduced pressure. No impurities (≤0.01 mass %) could be detected in BzOtBu by GC. For combustion experiments, the purified liquid samples were dried over molecular sieves and distilled once more before combustion. This procedure provided a colorless material, and the absence of water was shown by the Karl Fischer titration. For measurements of the energies of combustion of the BzOtBu, a rotating-bomb calorimeter described elsewhere[17] was used. The combus-

Table 2. Results from the Liquid-Phase Investigation of Equilibrium of Reactions 2−4 and Experimentally Determined Composition of Equilibrium Mixtures and Q_x−Values in the Liquid Phase, Calculated from Eqs 5 and 6[a]

T/K	n	x_{BzOH}	x_{BuOH}	x_{MB}	x_{2MB2}	x_{BuOtAm}	x_{BzOtAm}	$Q_x(2)$	$Q_x(3)$	$Q_x(4)$
298.2	6	0.1678		0.0687	0.0550		0.7084		76.8[b]	
	8	0.4987		0.0491	0.0321		0.4200		26.2	
	8	0.8065		0.0659	0.0060		0.1216		25.1	
303.4	4	0.2739	0.2144	0.0091	0.0493	0.2084	0.2448	0.917[b]	18.2	19.7[b]
	5	0.3197	0.2264	0.0204	0.0542	0.1087	0.2704	1.76	15.6	8.86
	8	0.7662		0.0327	0.0136		0.1875		18.0	
312.7	5	0.1964	0.6293	0.0054	0.0238	0.0991	0.0460	1.49	9.80	6.62
	3	0.2701	0.2193	0.0075	0.0789	0.2067	0.2175	0.854[b]	10.2	11.9[b]
313.2	5	0.0923		0.1026	0.2565		0.5486		23.2[b]	
	6	0.3114		0.0762	0.1525		0.4599		9.68	
	4	0.5777		0.0077	0.0571		0.3575		10.9	
	4	0.8367		0.0038	0.0177		0.1419		9.80	
322.4	6	0.2092	0.5095	0.0066	0.0442	0.1658	0.0646	0.952[b]	6.99	5.18
	6	0.1803	0.6502	0.0060	0.0311	0.1043	0.0381	1.31	6.80	5.16
323.2	4	0.6950		0.0069	0.0528		0.2452		6.68	
	5	0.8086		0.0076	0.0342		0.1495		5.41	
333.2	6	0.1380		0.1520	0.3800		0.3299		6.29[b]	
	6	0.3902		0.1020	0.2040		0.3038		3.81	
	3	0.6103		0.0127	0.1058		0.2712		4.20	
343.2	4	0.8447		0.0057	0.0360		0.1136		3.74	
	4	0.7246		0.0112	0.0905		0.1737		2.65	
	4	0.8372		0.0103	0.0509		0.1016		2.38	
	3	0.2252	0.5955	0.0075	0.0505	0.0908	0.0304	0.882	2.67	3.02
	5	0.3012	0.2891	0.0296	0.1600	0.1020	0.1181	1.11	2.45	2.21
353.2	6	0.3051		0.0988	0.2824		0.3136		3.63[b]	
	6	0.4272		0.0702	0.2340		0.2681		2.68[b]	
	3	0.6112		0.0289	0.1831		0.1768		1.59	
	4	0.8536		0.0056	0.0616		0.0792		1.51	
354.2	3	0.2164	0.6372	0.0067	0.0584	0.0632	0.0181	0.840	1.43	1.70
368.2	6	0.1184	0.4074	0.0350	0.2699	0.1374	0.0318	0.796	0.995	1.25
	5	0.2097	0.3584	0.0309	0.2396	0.1123	0.0490	0.746	0.975	1.32
371.2	3	0.6884		0.0221	0.184		0.1055		0.833	
	2	0.8469		0.0121	0.0860		0.0549		0.754	
373.2	6	0.4586		0.0832	0.2600		0.1982		1.66[b]	

[a] T is the temperature of investigation, n is number of determinations of composition within the time of equilibrium study, and x_i is the mole fraction determined chromatographically. [b] The value was not taken into account by calculation of the thermodynamic functions of reactions 2−4 because it did not meet the requirement ($x_{ROH} > 0.5$).

Table 3. Results for Typical Combustion Experiment at T = 298.15 K (p° = 0.1 MPa) for Benzyl *tert*-Butyl Ether[a]

m (substance)/g [b]	0.366423
m' (cotton)/g[b]	0.001003
m'' (polythen)/g[b]	0.558724
ΔT_c/K[c]	1.30070
$(\epsilon_{calor})(-\Delta T_c)$/J	−32654.11
$(\epsilon_{cont})(-\Delta T_c)$/J	−23.69
ΔU_{corr}/J[d]	16.30
$-m'\Delta_c u'$/J	17.00
$-m''\Delta_c u''$/J	25903.0
$\Delta_c u^\circ$ (substance)/(J·g^{-1})	−38753.9

[a] For the definition of the symbols, see ref 18: $T_h = 298.15$ K; V(bomb) = 0.2664 dm^3; p^i(gas) = 3.04 MPa; $m^i(H_2O)$ = 0.78 g; ΔU(ign) = 1.46 J; m(Pt) = 12.18 g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\epsilon_{cont})(-\Delta T_c) = (\epsilon^i_{cont})(T^i - 298.15\ K) + (\epsilon^f_{cont})(298.15\ K - T^f + \Delta T_{corr.})$. $\epsilon_{calor} = (25088.1 \pm 1.2)$ J·K^{-1}. [d] ΔU_{corr}, the correction to standard state, is the sum of items 81−85, 87−90, 93, and 94 in reference Hubbard et al.[18]

Table 4. Summary of Experimental Energies of Combustion of Benzyl *tert*-Butyl Ether and Standard Molar Thermodynamic Functions at T = 298.15 K (p° = 0.1 MPa)

[($\Delta_c u^\circ$)(benzyl *tert*-butyl ether, liquid, 298.15 K)]/(J·g^{-1})					
−38753.9	−38761.2	−38762.0	−38747.9	−38755.1	−38743.6

$\langle -\Delta_c u^\circ \rangle$/(J·g^{-1})	−38754.04 ± 3.0
$\Delta_c H^\circ_m$(l)/(kJ·mol^{-1})	−6374.0 ± 1.6
$\Delta_f H^\circ_m$(l)/(kJ·mol^{-1})	−241.3 ± 2.2

tion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The results are based upon the mass of sample burned. For converting the energy of the actual bomb process to that of an isothermal process and reducing to standard states, the conventional procedure[18] was applied. Results of a typical combustion experiment for BzOtBu and the mean values of the standard specific energies of combustion $\Delta_c u^\circ$, together with their standard deviations, are listed in the Tables 3 and 4. Standard enthalpy of combustion $\Delta_c H^\circ_m$ and standard enthalpy of formation $\Delta_f H^\circ_m$ of BzOtBu (see Table 4) were calculated according to the established procedure[18] using the molar enthalpies of formation for H_2O(l) and CO_2(g) as recommended by the IUPAC.[19] The assigned standard deviations of the mean values of $\Delta_f H^\circ_m$ include the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2.

2.4. Measurements of the Enthalpies of Vaporization Using the Transpiration Method. Vapor pressures and enthalpies of vaporization of BzOH and BzOtBu were determined using the method of transpiration in a saturated N_2 stream[20] and applying the Clausius−Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with a diameter of 1 mm provide a surface that is sufficient enough for the vapor−liquid equilibration. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube and the transported amount of gaseous material was collected in a cooling trap. The flow rate of the nitrogen stream was measured using a soap bubble flow meter and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. On one hand, the flow rate of the nitrogen stream in the saturation tube should not be too slow in order to avoid the transport of material from the U-tube due to diffusion. On the other hand, the flow rate should not be too fast in order to reach the saturation of the nitrogen stream with a compound. We tested our apparatus at different flow rates of the carrier gas in order to check the lower boundary of the flow below which the contribution of the vapor condensed in the trap by diffusion becomes comparable to the transpired one. In our apparatus, the contribution due to diffusion was negligible at a flow rate up to 0.11 cm^3·s^{-1}. The upper limit for our apparatus where the speed of nitrogen could already disturb the equilibration was at a flow rate of 1.5 cm^3·s^{-1}. Thus, we carried out the experiments in the flow rate interval of (0.28−0.52) cm^3·s^{-1}, which has ensured that the transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. The mass of compound collected within a certain time interval is determined by dissolving it in a suitable solvent with a certain amount of internal standard (hydrocarbon). This solution is analyzed using a gas chromatograph equipped with an autosampler. Uncertainty of the sample amount determined by GC analysis was assessed to be within 1−3%. The peak area of the compound related to the peak of the external standard (hydrocarbon n-C_nH_{2n+2}) is a direct measure of the mass of the compound condensed into the cooling trap provided a calibration run has been made. From this information, the vapor pressure of the compound under study can be determined, i.e., the ideal gas law can be applied provided that the vapor pressure of the substance is low enough. Real gas corrections arising from interactions of the vapor with the carrier gas turned out to be negligible. The saturation vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated

$$p_i^{\text{sat}} = m_i R T_a / V M_i$$

$$V = V_{N_2} + V_i$$

$$(V_{N_2} \gg V_i) \tag{7}$$

where $R = 8.31451$ J·K^{-1}·mol^{-1}, m_i is the mass of transported compound, M_i is the molar mass of the compound, and V_i is its volume contribution to the gaseous phase. V_{N_2} is the volume of transporting gas, and T_a is the temperature of the soap bubble meter. The volume of transporting gas V_{N_2} was determined from the flow rate and time measurements. Data of p_i^{sat} have been obtained as a function of temperature and were fitted using following equation[20]

$$R \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \tag{8}$$

where a and b are adjustable parameters and $\Delta_l^g C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phase, respectively. T_0 appearing in eq 8 is an arbitrarily chosen reference temperature (which has been chosen to be 298.15 K). Consequently, from eq 8 the expression for the vaporization enthalpy at temperature T is derived

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p T \tag{9}$$

Values of $\Delta_l^g C_p$ have been calculated according to a procedure developed by Chickos.[21−22] Experimental results and parameters a and b are listed in Table 5. The errors in the enthalpies of vaporization are calculated from eq 8 by using the method of least squares, and uncertainties in values of $\Delta_l^g C_p$ are not taken into account. We have checked experimental and calculation procedure with measurements of vapor pressures of n-alcohols.[20] It turned out that vapor pressures derived from the transpiration method were reliable within 1−3% and their accuracy was governed by reproducibility of the GC analysis.

Table 5. Vapor Pressures p and Vaporization Enthalpy, $\Delta_l^g H_m$, Obtained by the Transpiration Method

T	m	$V(N_2)$	p	N_2 flow	$(p_{\text{exp}} - p_{\text{calc}})$	$\Delta_l^g H_m$
K[a]	mg[b]	dm^3[c]	Pa[d]	cm^3·s^{-1}	Pa	kJ·mol^{-1}
Benzyl Alcohol						
$\ln(p/\text{Pa}) = \frac{309.1}{R} - \frac{85822.6}{R(T/\text{K})} - \frac{66.7}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
282.9	0.664	5.00	3.06	1.11	0.06	66.96
285.9	0.698	3.94	4.07	0.82	0.02	66.76
288.9	0.726	3.13	5.32	0.33	−0.10	66.56
292.1	0.753	2.34	7.38	1.11	0.04	66.34
295.3	0.822	1.91	9.83	0.82	−0.03	66.13
298.2	0.801	1.46	12.51	1.11	−0.30	65.94
301.2	0.746	1.04	16.45	0.82	−0.24	65.74
302.8	0.917	1.09	19.23	0.82	0.06	65.63
305.8	0.746	0.671	25.41	0.33	0.66	65.43
308.8	0.733	0.524	31.92	0.82	0.15	65.23
311.7	0.808	0.461	39.99	0.33	−0.24	65.04
314.9	0.760	0.335	51.72	0.15	−0.18	64.82
318.1	0.801	0.272	67.09	0.33	0.53	64.61
321.1	0.767	0.210	83.48	0.15	−0.11	64.41
Benzyl *tert*-Butyl Ether						
$\ln(p/\text{Pa}) = \frac{327.9}{R} - \frac{89455.8}{R(T/\text{K})} - \frac{108.0}{R}\ln\left(\frac{T/\text{K}}{298.15}\right)$						
277.8	0.430	1.29	5.12	0.22	0.01	59.45
278.1	1.232	3.56	5.28	0.82	0.05	59.43
279.1	1.102	2.90	5.77	0.82	0.03	59.32
281.3	1.507	3.27	6.98	0.82	−0.03	59.08
282.9	0.440	0.830	7.97	0.22	−0.15	58.90
284.3	1.428	2.41	8.93	0.82	−0.21	58.76
286.2	1.428	1.96	10.95	0.82	0.17	58.55
287.3	1.473	1.88	11.77	0.82	−0.07	58.43
287.8	0.700	0.870	12.09	0.22	−0.32	58.37
288.2	1.552	1.78	13.10	0.82	0.32	58.34
290.0	1.417	1.43	14.85	0.82	−0.02	58.14
292.2	1.417	1.17	18.20	0.82	0.38	57.90
293.0	0.980	0.780	18.88	0.22	−0.21	57.81
293.2	1.642	1.29	19.08	0.82	−0.25	57.80
295.2	1.518	0.982	23.12	0.82	0.44	57.58
296.2	1.338	0.818	24.45	0.82	−0.11	57.47
297.2	1.271	0.716	26.52	0.82	−0.04	57.36
298.0	0.810	0.430	28.43	0.22	0.05	57.27
298.2	2.002	1.02	29.24	0.82	0.53	57.26
299.2	1.394	0.675	30.85	0.82	−0.16	57.15
300.3	1.406	0.614	34.19	0.82	0.46	57.03
302.2	1.541	0.593	38.75	0.82	−0.18	56.82
303.1	0.830	0.300	41.77	0.22	−0.02	56.72
303.2	1.653	0.573	43.05	0.82	1.10	56.72
308.0	1.000	0.260	57.54	0.22	−2.15	56.19

[a] Temperature of saturation. [b] Mass of transferred sample, condensed at $T = 243$ K. [c] Volume of nitrogen, used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at $T = 243$ K.

Table 6. Enthalpies $\Delta_r H^\circ_m$ of Reactions 1−4 in the Liquid Phase at T = 298.15 K, Coefficients A and B of the Temperature Dependence of the Equilibrium Ratios $\ln Q_x = A + B(T/K)^{-1}$, and Standard Enthalpy of Formation of Benzyl Alcohol in the Liquid State at 298.15 K Derived from Enthalpies of Reactions 1, 2, and 3, Respectively (See Text)

	$\langle T\rangle$[a]	$\Delta_r H^\circ_m$[b]	$\ln Q_x = A + B\cdot(T/K)^{-1}$		$\Delta_r H^\circ_{m(l,BzOH)}$
reaction	K	kJ·mol^{-1}	A	B	kJ·mol^{-1}
1	332.5	−9.9 ± 0.4	−3.2	1187.0	−155.1 ± 2.9
2	335.8	−12.1 ± 0.9	−4.2	1453.7	−154.7 ± 3.9
3	335.7	−42.7 ± 1.1	−14.1	5138.2	−153.0 ± 3.5
	337.3[c]	−42.7 ± 1.4[c]	−14.0[c]	5130.7[c]	
4	335.8	−28.5 ± 2.0	−9.1	3422.6	
	345.7[d]	−28.1 ± 0.8[c]	−8.9[c]	3384.5[c]	

[a] The average temperature of the equilibrium study. [b] Derived from the temperature dependence of Q_x for $x_{ROH} > 0.5$. [c] Results from our previous work.10 [d] Results from our previous work.11

3. Results and Discussion

3.1. Equilibrium Constants and Reaction Enthalpies. The experimental results of chemical equilibrium study of the reactions 1−4 are listed in Tables 1 and 2. It is well established that reactive mixtures of the *tert*-alkyl ethers synthesis behave strongly nonideally, especially when the mole fractions of alkanol are low.[11−16] On this basis, the activity coefficients γ_i should be used to calculate the true thermodynamic equilibrium constant K_a. However, in our previous works,[11−16] we developed a procedure to determine $\Delta_r H^\circ_m$ for etherification reactions from experimental data of Q_x (according to eqs 5 and 6) without measuring activity coefficients γ_i of the reactants. Because we observed that Q_x values are almost independent of the mole fraction of alcohol if $x_{ROH} > 0.5$, it was suggested that Q_x values in this concentration range are close to the true thermodynamic equilibrium constant K_a. Under this assumption, experimental values of Q_x could be approximated as a function of temperature by the linear equation $\ln Q_x(x_{ROH} > 0.5) = A + B(T/K)^{-1}$ using the method of least squares. The slope of this line when multiplied by the gas constant yields the enthalpy of reaction, $\Delta_r H^\circ_m$. We tested this procedure for numerous etherification reactions.[11−16] In all cases, the enthalpy of reaction calculated from Q_x values measured for the mole fraction of alcohol $x_{ROH} > 0.5$ (according to the *Second Law*) was in excellent agreement with those $\Delta_r H^\circ_m$ calculated using enthalpies of formation derived from combustion calorimetry (according to the *First Law*). In this work, we applied this simplified procedure to the reactions 1−4 and derived their $\Delta_r H^\circ_m$ from Q_x values determined for the mole fraction of alcohol $x_{ROH} > 0.5$ according to the *Second Law*. Numerical results are presented in Table 6. The errors in the thermodynamic functions from equilibrium study are given by the standard deviations from the linear equation $\ln Q_x(x_{ROH} > 0.5) = A + B(T/K)^{-1}$ for the level of confidence of 95%.

Equilibrium of reaction 1 (see Table 1) was investigated from both sides − using initial liquid mixtures of BzOH with BuOtBu, as well as with initial mixtures of BzOtBu and BuOH. Small amounts of *iso*-butene as a byproduct were detected in the reacting mixture. It was not possible to measure this amount reproducibly, because it escaped during analytical procedure very rapidly.

Equilibrium of reaction 2 (see Table 2) was investigated using initial liquid mixtures of BzOH with BuOtAm. Certain amounts of methyl-butenes were detected in the reacting mixture. These olefins alkylated BzOH and BuOH, and due to this reason, reactions 3 and 4 reached equilibrium parallel to the reaction 2 (by using initial liquid mixtures of BzOH with BuOtAm). Equilibrium constants for all three reactions are listed in Table 2. To prove whether Q_x of reaction 3 depends on reacting mixture content, the latter reaction was studied using initial liquid mixtures of BzOH with 2MB2. Thus, in this case, the reacting mixture consisted from BzOH, BzOtAm, and methyl-butenes. However, Q_x values of reaction 3 measured in this system for the mole fraction of alcohol $x_{ROH} > 0.5$ (see Table 2) were indistinguishable with those measured in the presence of BuOH and BuOtAm and were treated together. The experimental values of Q_x of the reaction 4 measured in this work (in the presence of BzOH and BzOtAm), as well as the enthalpy of this reaction, are also in very close agreement (see Table 6) with those obtained by direct alkylation of BuOH with methyl-butenes.[11]

The chemical equilibrium of the reactive systems 1−4 was studied in the liquid phase in the temperature range (298 to 373) K. Although equilibrium studies have been performed at elevated temperatures, the corrections of the enthalpies of reactions 1−4 are assessed to be less than (0.3−0.5) kJ·mol^{-1} according to our estimations with help of heat capacities of the reaction participants collected in the database.[22] In further calculations, it was assumed that the enthalpies of reactions 1−4 hardly change on passing from the average temperature of the experimental range to T = 298.15 K.

3.2. Enthalpy of Formation of Benzyl Alcohol in the Liquid Phase. We investigated the chemical equilibrium of reactions 1−3 and derived the enthalpy of this reaction in the liquid phase. The enthalpy of formation $\Delta_f H^\circ_{m(l)}$ of *tert*-butyl benzyl ether at 298.15 K was measured by means of combustion calorimetry in this work (see Table 4). The latter value, as well as enthalpies of reactions 1−3 (see Table 6), was involved in the calculation of the standard enthalpies of formation of the benzyl alcohol. For this purpose, standard molar enthalpies of formation, $\Delta_f H^\circ_{m(l,298.15K)}$, of 2-methylbutene-2, tert-alkyl ethers, and butan-1-ol are required. Enthalpy of formation in the liquid phase of 2-methylbut-2-ene, $\Delta_f H^\circ_{m(l)} = -(68.1 \pm 1.3)$ kJ·mol^{-1}, was taken from combustion experiments.[23] Experimental data for *tert*-alkyl ethers have been reviewed recently,[24] and values for BuOtBu, $\Delta_f H^\circ_{m(l)} = -(403.3 \pm 1.9)$ kJ·mol^{-1}, for BuOtAm $\Delta_f H^\circ_{m(l)} = -(424.0 \pm 2.4)$ kJ·mol^{-1}, and for BzOtAm $\Delta_f H^\circ_{m(l)} = -(263.8 \pm 3.0)$ kJ·mol^{-1} were taken from this source. Data for butan-1-ol $\Delta_f H^\circ_{m(l)} = -(327.0 \pm 0.2)$ kJ·mol^{-1} were taken from Mosselman and Dekker.[25] These data were used to calculate the enthalpy of formation of benzyl alcohol in the liquid phase (e.g., for the reaction 1)

$$\Delta_f H^\circ_{m(l,BzOH)} = -\Delta_r H^\circ_{m(1)} + \Delta_f H^\circ_{m(l,BzOtBu)} + \Delta_f H^\circ_{m(l,BuOH)} - \Delta_f H^\circ_{m(l,BuOtBu)} = -(155.1 \pm 2.9)\ \mathrm{kJ\ mol^{-1}}$$

In a similar way, $\Delta_f H^\circ_{m(l,BzOH)}$ was calculated from data for reactions 2 and 3 (see Table 6). All three values are in very close agreement to the recent result from Papina et al.[6] $\Delta_f H^\circ_{m(l,BzOH)} = -(154.9 \pm 3.0)$ kJ mol^{-1} measured by

Table 7. Comparison of Data for the Enthalpy of Vaporization[a] of Benzyl Alcohol at 298.15 K

technique	T/K	$\Delta_l^g H_m$ at T = 298.15 K/kJ·mol^{-1}	ref
ebulliometr	not specified	60.29 ± 0.42	Mathews, 1926[28,27]
ebulliometr	312.0−424.8	63.0 ± 2.2	Gardner, 1937[35]
ebulliometr	395.7−478.6	62.08 ± 0.27	Dreisbach, 1949[34]
ebulliometr	312−397	65.4 ± 2.0[b]	Belina, 1974[32]
transpiration	302.6−333.2	66.8 ± 1.4[b]	Grayson, 1982[33]
not specified	385−573	62.7	Stephenson, 1987[37]
not specified	293−313	61.8	Stephenson, 1987[37]
ebulliometr	404.1−507.4	62.46 ± 0.30[b]	Ambrose, 1990[29]
transpiration	277.4−318.2	64.82 ± 0.64[b]	Verevkin, 1999[30]
transpiration	282.2−323.0	65.46 ± 0.38[b]	Vasiltsova, 2004[31]
transpiration	282.9−321.1	65.94 ± 0.24[b]	this work
average		65.75 ± 0.51[c]	this work

[a] Vapor pressure available in the literature were treated using eqs 8 and 9 in order to calculate enthalpy of vaouorization at 298.15 K in the same way as our own results from Table 5. [b] Values selected to calculate average enthalpy of vaporization. [c] Average value (was calculated taking into consideration the uncertainty as a statistical weighting factor[26]) recommended for calculation of gaseous enthalpy of formation of benzyl alcohol.

combustion calorimetry. Taking into account such close agreement, we calculated the average from 4 values taking into consideration the uncertainty as a statistical weighting factor,[26] and the average value $\Delta_f H^\circ_{m(l,BzOH)} = -(154.5 \pm 1.7)$ kJ·mol^{-1} at 298.15 K could be recommended.

3.3. Enthalpy of Vaporization of Benzyl Alcohol and Benzyl tert-Butyl Ether at 298.15 K. Vapor pressure and enthalpy of vaporization $\Delta_l^g H_m = (57.26 \pm 0.28)$ kJ·mol^{-1} of BzOtBu have been measured for the first time. Enthalpies of vaporization of benzyl alcohol derived from the vapor pressure measurements using eqs 7 and 8 are collected in Table 7. Pedley et al.[27] reanalyzed the earliest value of $\Delta_l^g H_m = (50.50 \pm 0.04)$ kJ·mol^{-1} reported in the literature[28] and calculated $\Delta_l^g H_m = (60.29 \pm 0.42)$ kJ·mol^{-1}. The most reliable measurements of the $p-T$ data for benzyl alcohol were performed by Ambrose and Ghiasse,[29] using ebulliometry in the temperature range 404.1−507.4 K. However, a long way of extrapolation of their vaporization enthalpy over 150 K to the reference temperature 298.15 K is accompanied with the large uncertainty. Our first result[30] $\Delta_l^g H_m = (64.8 \pm 0.6)$ kJ·mol^{-1} was essentially different from most of the earlier investigations (see Table 7). This fact has prompted us to ascertain vapor pressure measurements on BzOH by the transpiration method. However, our recent result[31] $\Delta_l^g H_m = (65.5 \pm 0.4)$ kJ·mol^{-1} was in agreement to previous determination within the boundaries of experimental uncertainties. In this work, the most attention has been played to a proof of saturation conditions during the transpiration experiment (by variation of nitrogen stream speed) in a broad range (see Table 7). Nevertheless, this latest and somewhat more precise result (65.94 ± 0.24) kJ·mol^{-1} (Table 7) was again in close agreement with our previous determinations as well as with the results from refs 32 and 33, which were obtained in the similar to ours temperature ranges. We selected these two results[32,33] and together with three of our own values used them to calculate average value of enthalpy of vaporization of benzyl alcohol $\Delta_l^g H_m(298.15\ \text{K}) = (65.75 \pm 0.51)$ kJ·mol^{-1} taking into consideration the uncertainty as a statistical weighting factor.[26]

3.4. Enthalpy of Formation of Benzyl Alcohol in the Gaseous Phase at 298.15 K. Average values of enthalpy of vaporization $\Delta_l^g H_m$ and enthalpy of formation $\Delta_f H^\circ_{m(l)}$ of benzyl alcohol have allowed us to derive $\Delta_f H^\circ_{m(g)} = -(88.8 \pm 1.8)$ kJ·mol^{-1} for this compound. An independent way to obtain support for this result serves the enthalpy of reaction of dehydrogenation of benzyl alcohol

$$\text{benzyl alcohol} \leftrightarrow \text{benzaldehyde} + H_2$$

$\Delta_r H^\circ_m(298.15\ \text{K}) = 53.93$ kJ·mol^{-1}, measured by Cubberley and Mueller[36] in the gaseous phase using equilibrium technique. With the help of the $\Delta_f H^\circ_{m(g)} = -(36.7 \pm 2.9)$ kJ·mol^{-1} of benzaldehyde (Pedley et al.),[27] we estimated the gaseous enthalpy of formation $\Delta_f H^\circ_{m(g)} = -90.6$ kJ·mol^{-1} of benzyl alcohol. This value is in close agreement with those from our recommendations. Concordance of the data obtained from different sources supports the correctness of the values of $\Delta_f H^\circ_{m(g)} = -(88.8 \pm 1.8)$ kJ·mol^{-1}, $\Delta_l^g H_m = (65.75 \pm 0.51)$ kJ·mol^{-1}, and $\Delta_f H^\circ_{m(l)} = -(154.5 \pm 1.7)$ kJ·mol^{-1} for benzyl alcohol at 298.15 K recommended for the further thermochemical calculations. Quantification of the hydrogen bond strength in benzyl alcohol, with help of gaseous enthalpy of formation obtained in this work, will be reported in our next paper.

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