Chemical Equilibrium Study in the Reacting System of the (1-Alkoxyethyl)benzene Synthesis from Alkanols and Styrene

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The chemical equilibrium of the reactive system alkanol + styrene ⇔ (1-alkoxyethyl)benzene (where alkyl is methyl, ethyl, propyl, and butyl) was studied in the liquid phase in the temperature range (343 to 423) K using a cation exchanger as the heterogeneous catalyst. Enthalpies of reactions $\Delta_r H^o_m$ of (1-alkoxyethyl)benzene synthesis in the liquid phase were obtained from the temperature dependence of equilibrium constants measured in the reactive mixtures with an excess of alkanol and showed a good agreement with those reaction enthalpies derived from values of the enthalpies of formation $\Delta_f H^o_m$(l) of the reactions participants measured for (1-methoxyethyl)benzene and (1-butoxyethyl)benzene by combustion calorimetry. The standard molar enthalpies of vaporization of (1-alkoxyethyl)benzenes were obtained from the temperature dependence of the vapor pressure measured by using the transpiration method. Resulting values of $\Delta_f H^o_m$(g) were used to prove the consistency of the experimental data and to derive strain enthalpies of (1-alkoxyethyl)benzenes. The strain effects were discussed in terms of deviations of $\Delta_f H^o_m$(g) from the group additivity rules.

1. Introduction

Aliphatic ethers are extensively used in gasolines to reduce evaporative and tail-pipe emissions and as an octane number improver. Their growing demand has promoted the evaluation of suitable ethers. Besides widely used methyl *tert*-butyl ether and *tert*-amyl methyl ether, further candidates are (1-alkoxyethyl)benzenes synthesized in the liquid phase over acid-functionalized ion-exchanged resin catalysts from alkanols and styrene (see Figure 1). Styrene and alkanols are large-scale products of the chemical industry, and their chemical reactions provide yields of the ethers of over 50 mol %. Therefore, (1-alkoxyethyl)benzenes are promising substances for the aforementioned purpose. As an extension of our previous works,[1,2] we have performed a systematic investigation of the chemical equilibrium in the reacting systems of the (1-alkoxyethyl)benzene synthesis such as methyl (MeEB), ethyl (EtEB), propyl (PrEB), and butyl (BuEB) derivatives (see Figure 1). New experimental data of the reaction enthalpies are reported. Values of $\Delta_f H^o_m$(l) were derived from the temperature dependence of equilibrium constants measured in the reactive mixtures with an excess of alkanol. To prove the validity of the procedure used, these results are compared with those calculated from differences of the enthalpies of formation of the reaction participants. For this purpose, standard molar enthalpies of formation in the liquid phase $\Delta_f H^o_m$(l) of (1-methoxyethyl)benzene and (1-butoxyethyl)benzene were additionally obtained from calorimetrically measured enthalpies of combustion. Further support of the reliability of the procedures applied in this work is expected from the quantitative analysis of standard molar enthalpies of formation in the gaseous phase $\Delta_f H^o_m$(g). Values of $\Delta_f H^o_m$(g) of (1-alkoxyethyl)benzenes were obtained from calorimetrically measured $\Delta_f H^o_m$(l) and their enthalpies of vaporization measured by a transpiration method. Thus, the systematic investigation of the (1-alkoxyethyl)benzene synthesis reactions would be of value for two reasons. First, if good agreement between the standard reaction enthalpies $\Delta_r H^o_m$(l), obtained from the temperature dependence of the equilibrium constants, and those obtained from combustion calorimetry is found, it would confirm that the reliability and accuracy of our procedures is satisfactory. Second, experimental values $\Delta_f H^o_m$(g) would provide useful information on the strain effects and the relation between the structure and properties of (1-alkoxyethyl)benzenes. The results of the study can also contribute to an improvement of the group contribution methodology.

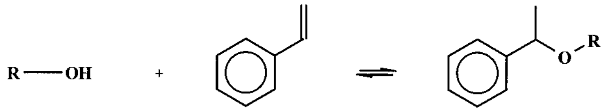

Figure 1. Reaction of the (1-alkoxyethyl)benzene synthesis (R = CH_3, C_2H_5, C_3H_7, and C_4H_9).

2. Experimental Section

2.1. Materials. Styrene, methanol (MeOH), ethanol (EtOH), propan-1-ol (PrOH), and butan-1-ol (BuOH) (water content less than 0.01%) were purchased from Merck. Gas chromatograph (GC) analyses gave a purity of >99.9%, in agreement with specifications. (1-Alkoxyethyl)benzenes (Figure 1) were synthesized via alkylation of an appropriate alkanol with styrene in the presence of a catalytic amount of cation-exchange resin in H^+ form (Amberlist 15, Aldrich) at 343 K. Prior to the experiments the cation-exchange resin Amberlist 15 in H^+ form was dried 8 h at 383 K in a vacuum oven at reduced pressure.

The pure samples of (1-alkoxyethyl)benzenes were obtained by repeated distillations at reduced pressure under N_2, after being dried with molecular sieves (0.4 nm). No impurities (greater than mass fraction 10^{-4}) could be detected in the samples by GC.

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2.2. Chemical Equilibrium Study. Glass vials with screwed caps were filled two-thirds full with the initial liquid mixture of alkanol and styrene. Cation-exchange resin Amberlist 15 (Aldrich) in H^+ form was added as a solid catalyst. The quantity of catalyst was approximately 10% from the mass of the mixture. The vial was thermostated at temperature $T_i \pm 0.1$ 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. Thermostating of the vial was then continued at the same temperature. Samples were withdrawn until no further change of the compositions was observed, indicating that the chemical equilibrium was established.

The compositions of the reaction mixtures were analyzed with a Hewlett-Packard gas chromatograph 5890 series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 $cm^3 \cdot s^{-1}$. 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. The standard temperature program of the GC was $T = 353$ K for 180 s followed by a heating rate of 0.167 $K \cdot s^{-1}$ to $T = 523$ K. Response factors of all reagents were determined using calibration mixtures of the corresponding components prepared gravimetrically.

2.3. Combustion Calorimetry. An isoperibolic calorimeter[1,2] equipped with a static bomb and an isothermal water jacket was used for measuring the energies of combustion of (1-methoxyethyl)benzene and (1-butoxyethyl)benzene. The temperature of the water jacket was maintained to within ±0.0015 K using a high-precision mercury-contact thermometer. To exclude traces of water in the liquid samples used for the combustion experiments, the purified samples were dried over molecular sieves and distilled once more prior to combustion. Each sample was sealed in a container to avoid oxidation and contamination with moisture. In the present study, we used commercially available polythene ampules (Fa. NeoLab, Heidelberg) of 1 cm^3 volume as the sample container for liquids. The initial temperature of the combustion experiments was 298.15 K for each experiment. The energy equivalent of the calorimeter ϵ_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39i, NIST). From seven experiments, ϵ_{calor} was measured to be 15 296.0 ± 2.3 $J \cdot K^{-1}$. For conversion of the energy of the actual bomb process to that of the isothermal process and reduction to standard states, the conventional procedure[3,4] was applied. The sample masses of (1-alkoxyethyl)benzenes were reduced to vacuum, taking into consideration the density value $\rho_{293} = 0.941$ $g \cdot cm^{-3}$ for the MeEB and $\rho_{293} = 0.910$ $g \cdot cm^{-3}$ for the BuEB, which were determined in a calibrated 10 cm^3 pycnometer. The energies of combustion of the cotton thread, $\Delta_c u°(CH_{1.774}O_{0.887}) = -(16\,945.2 \pm 4.2)$ $J \cdot g^{-1}$, and polythene, $\Delta_c u°(CH_{1.930}) = -46\,361.0 \pm 3.1$ $J \cdot g^{-1}$, were measured in our laboratory earlier.

Table 1. Experimentally Determined Composition of Equilibrium Mixtures and K_X Values in the Liquid Phase, Calculated from Eq 1 for the System Methanol + Styrene ⇔ (1-Methoxyethyl)benzene[a]

T (K)	n	x_{MeOH}	$x_{Styrene}$	x_{MeEB}	K_X[b]
343.1	12	0.0934	0.1666	0.7400	47.52 ± 0.63
	11	0.2422	0.0792	0.6786	35.35 ± 0.52
	13	0.3145	0.0857	0.5998	22.25 ± 0.42
	10	0.5813	0.0374	0.3813	17.53 ± 0.46[c]
	11	0.7214	0.0201	0.2585	17.83 ± 0.19[c]
353.1	12	0.2602	0.1013	0.6385	24.23 ± 0.48
	12	0.3875	0.0847	0.5278	16.08 ± 0.39
	11	0.6577	0.0327	0.3095	14.37 ± 0.31[c]
	13	0.7720	0.0193	0.2087	14.02 ± 0.42[c]
373.1	12	0.1236	0.1756	0.7007	32.27 ± 0.56
	10	0.2728	0.1118	0.6154	20.19 ± 0.48
	11	0.3701	0.0923	0.5376	15.73 ± 0.37
	12	0.6614	0.0494	0.2892	8.85 ± 0.26[c]
	10	0.7861	0.0272	0.1867	8.72 ± 0.28[c]
	10	0.8579	0.0171	0.1250	8.52 ± 0.38[c]
403.1	12	0.2514	0.1665	0.5821	13.90 ± 0.66
	9	0.5537	0.1244	0.3219	4.67 ± 0.57[c]
	13	0.6769	0.0697	0.2535	5.37 ± 0.29[c]
	10	0.7706	0.0457	0.1836	5.21 ± 0.25[c]
423.1	12	0.2415	0.2005	0.5580	11.52 ± 0.42
	12	0.4746	0.2065	0.3189	3.25 ± 0.33[c]
	10	0.6508	0.1040	0.2452	3.62 ± 0.25[c]
	12	0.8119	0.0523	0.1358	3.20 ± 0.22[c]

[a] T is the temperature of the investigation; n is the number of determinations of composition within the time of the equilibrium study; x_i is the mole fraction measured chromatographically. [b] Uncertainity is the standard deviation. [c] Values involved in the determination of the enthalpy of reaction.

2.4. Transpiration Method. The enthalpies of vaporization of the (1-alkoxyethyl)benzenes were determined using the method of transpiration in a saturated N_2 stream and applying the Clausius−Clapeyron equation. The method has been described before[1,2] and has proven to give results in excellent agreement with other established techniques for determining vapor pressures of pure substances and enthalpies of vaporization from the temperature dependence of the vapor pressure. About 0.5 g of the sample was mixed with glass beads (having a size of 1 mm) and placed in a thermostated U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. A nitrogen stream was passed through the U tube at constant temperature (±0.1 K), and the transported amount of gaseous material was collected in a cold trap. The flow rate of the nitrogen stream (0.28 to 0.56) $cm^3 \cdot s^{-1}$ was measured using a soap bubble flowmeter and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The amount of condensed substance was determined by GC analysis using an internal standard (hydrocarbon n-$C_{11}H_{24}$). The saturation vapor pressure at each temperature T_i was calculated from the amount of product collected within a definite period of time. With the assumption of Dalton's law of partial pressures applied to the saturated nitrogen stream, values of p were calculated by assuming the validity of the ideal gas law:

$$p = mRT_a/V(N_2)\,M \qquad (1)$$

where $R = 8.314\,51$ $J \cdot K^{-1} \cdot mol^{-1}$; m is the mass of transported compound; $V(N_2)$ is the volume of transporting gas; M is the molar mass of the compound; and T_a is the ambient temperature. The volume of transporting gas $V(N_2)$ was determined from the flow rate and time measurements. The flow rate was maintained constant with the help of the high-precision needle valve (Hoke, C1335G6 MM-ITA). The accuracy of the volume $V(N_2)$ measurements from flow rate was established as ±0.001 dm^3 with the help of a series of experiments, where the volume of the nitrogen was measured with a gas clock or by water withdrawn from a calibrated gasometer. Because the nitrogen stream was measured using a soap bubble flowmeter at ambient temperature, this temperature was applied for the calculation of the vapor pressure p according to eq 1. The vapor pressure p at each saturation temperature was calculated from the mass of product collected within a definite time period, and the small value of the residual vapor pressure of a compound at the temperature of condensation was

Table 2. Experimentally Determined Composition of Equilibrium Mixtures and K_X Values in the Liquid Phase, Calculated from Eq 1 for the System Ethanol + Styrene ⇔ (1-Ethoxyethyl)benzene[a]

T (K)	n	x_{EtOH}	$x_{Styrene}$	x_{EtEB}	K_X[b]
343.1	12	0.0915	0.2000	0.7085	38.73 ± 0.69
	10	0.1720	0.1886	0.6394	19.71 ± 0.82
	9	0.6215	0.0519	0.3266	10.12 ± 0.43[c]
	13	0.7702	0.0249	0.2049	10.68 ± 0.56[c]
353.1	16	0.2368	0.1360	0.6272	19.48 ± 0.69
	12	0.3266	0.1271	0.5463	13.16 ± 0.33
	11	0.6523	0.0521	0.2956	8.70 ± 0.33[c]
	12	0.8061	0.0243	0.1695	8.64 ± 0.32[c]
373.1	8	0.1765	0.2236	0.5999	15.19 ± 0.65
	8	0.3751	0.1644	0.4606	7.47 ± 0.39
	10	0.5299	0.1206	0.3495	5.47 ± 0.21[c]
	9	0.7806	0.0418	0.1776	5.44 ± 0.24[c]
	11	0.8388	0.0271	0.1341	5.90 ± 0.26[c]
	7	0.9008	0.0158	0.0833	5.84 ± 0.26[c]
403.1	11	0.5198	0.1782	0.3020	3.26 ± 0.18[c]
	13	0.7776	0.0629	0.1595	3.26 ± 0.14[c]
	12	0.8439	0.0414	0.1147	3.28 ± 0.15[c]
423.1	10	0.5109	0.2182	0.2709	2.43 ± 0.13[c]
	12	0.7550	0.0896	0.1544	2.30 ± 0.13[c]
	11	0.8405	0.0528	0.1067	2.40 ± 0.13[c]

[a] T is the temperature of the investigation; n is the number of determinations of composition within the time of the equilibrium study; x_i is the mole fraction measured chromatographically. [b] Uncertainity is the standard deviation. [c] Values involved in the determination of the enthalpy of reaction.

Table 3. Experimentally Determined Composition of Equilibrium Mixtures and K_X Values in the Liquid Phase, Calculated from Eq 1 for the System Propanol + Styrene ⇔ (1-Propoxyethyl)benzene[a]

T (K)	n	x_{PrOH}	$x_{Styrene}$	x_{PrEB}	K_X[b]
353.1	11	0.2766	0.1297	0.5937	16.54 ± 0.28
	12	0.4223	0.0997	0.4780	11.35 ± 0.18[c]
	9	0.5542	0.0617	0.3841	11.24 ± 0.21[c]
	10	0.7270	0.0303	0.2427	11.02 ± 0.32[c]
373.1	10	0.3460	0.1475	0.5065	9.93 ± 0.25
	10	0.4426	0.1218	0.4356	8.08 ± 0.13[c]
	11	0.5702	0.0763	0.3525	8.09 ± 0.15[c]
	12	0.7410	0.0373	0.2217	8.02 ± 0.13[c]
393.1	8	0.4358	0.1605	0.4037	5.77 ± 0.15[c]
	13	0.5542	0.1113	0.3345	5.42 ± 0.11[c]
	10	0.7441	0.0517	0.2041	5.31 ± 0.14[c]
413.1	12	0.5722	0.1413	0.2843	3.52 ± 0.04[c]
	10	0.7093	0.0853	0.2054	3.40 ± 0.11[c]
	11	0.7844	0.0555	0.1601	3.67 ± 0.08[c]

[a] T is the temperature of the investigation; n is the number of determinations of composition within the time of the equilibrium study; x_i is the mole fraction measured chromatographically. [b] Uncertainity is the standard deviation. [c] Values involved in the determination of the enthalpy of reaction.

Table 4. Experimentally Determined Composition of Equilibrium Mixtures and K_X Values in the Liquid Phase, Calculated from Eq 1 for the System Butanol + Styrene ⇔ (1-Butoxyethyl)benzene[a]

T (K)	n	x_{BuOH}	$x_{Styrene}$	x_{BuEB}	K_X[b]
	11	0.3154	0.0930	0.5916	20.17 ± 0.43
353.1	10	0.5913	0.0406	0.3681	15.33 ± 0.41[c]
	13	0.6285	0.0349	0.3365	15.33 ± 0.49[c]
	12	0.8163	0.0132	0.1705	15.87 ± 0.42[c]
	10	0.9048	0.0064	0.0888	15.25 ± 0.36[c]
373.1	12	0.3314	0.1323	0.5363	12.23 ± 0.48
	9	0.4756	0.0966	0.4277	9.31 ± 0.37[c]
	10	0.5555	0.0708	0.3737	9.50 ± 0.31[c]
	11	0.6186	0.0538	0.3276	9.84 ± 0.27[c]
	12	0.8463	0.0172	0.1365	9.37 ± 0.26[c]
393.1	12	0.4403	0.1551	0.4046	5.93 ± 0.17[c]
	10	0.5283	0.1091	0.3625	6.28 ± 0.19[c]
	11	0.6327	0.0768	0.2905	5.98 ± 0.16[c]
	13	0.7945	0.0352	0.1702	6.08 ± 0.14[c]
413.1	10	0.5485	0.1293	0.3222	4.54 ± 0.15[c]
	12	0.7706	0.0532	0.1762	4.30 ± 0.16[c]
	12	0.8408	0.0322	0.1259	4.65 ± 0.13[c]

[a] T is the temperature of the investigation; n is the number of determinations of composition within the time of the equilibrium study; x_i is the mole fraction measured chromatographically. [b] Uncertainity is the standard deviation. [c] Values involved in the determination of the enthalpy of reaction.

added. The latter was calculated from a linear correlation between $\ln(p)$ and T^{-1} obtained by iteration. Results of the vapor pressure measurements as a function of temperature are shown in Table 8. The molar enthalpies of vaporization were calculated from the slope of the Clausius−Clapeyron correlation: $\Delta_l^g H_m^o = -R(\mathrm{d}\ln p/\mathrm{d}T)$. To derive $\Delta_l^g H_m^o(T)$ at the mean temperature $\langle T \rangle$ of the experimental temperature range, the integrated form of the linear Clausius−Clapeyron equation

$$\ln(p/\mathrm{Pa}) = a - b(T/\mathrm{K})^{-1} \qquad (2)$$

was used, where $b = \Delta_l^g H_m^o(T)\, R^{-1}$. The observed enthalpies of vaporization $\Delta_l^g H_m^o(T)$ at the mean temperature $\langle T \rangle$ obtained by this procedure are listed in Table 8 together with the coefficients a and b according to eq 2. The experimental data were approximated with the linear equation $\ln(p) = f(T^{-1})$ (see Table 8) using the method of least squares. The error in the enthalpy of vaporization at $\langle T \rangle$ was defined as the average deviation of experimental $\ln(p)$ from this linear correlation.

3. Results

3.1. Equilibrium Constants and Reaction Enthalpies. The experimental results of the chemical equilibrium study of the (1-alkoxyethyl)benzene synthesis are listed in Tables 1−4. As in the similar reaction systems[1,2] of alkyl cumyl ether synthesis from alkanol and α-methylstyrene (α-MS) studied previously,[1,2] we have used the equilibrium ratio K_X defined as

$$K_X = \frac{x_{\mathrm{Ether}}}{x_{\mathrm{Alkanol}}\, x_{\mathrm{Styrene}}} \qquad (3)$$

for characterizing the chemical equilibrium: x_i values in eq 3 are the mole fractions of reaction participants in the liquid phase. K_X depends strongly on the composition of the equilibrium mixture. The thermodynamic equilibrium constant K_a in the liquid phase is related to K_X by the following equation:

$$K_a = \frac{\gamma_{\mathrm{Ether}}}{\gamma_{\mathrm{Alkanol}}\gamma_{\mathrm{Styrene}}} \cdot K_X \qquad (4)$$

where γ_i is the activity coefficient of component i depending on the mixture composition. In our previous work[1] we investigated the chemical equilibrium in the liquid and gaseous phase of the methyl cumyl ether synthesis reaction. We performed a set of experiments to determine the thermodynamic equilibrium constants and reaction enthalpies in the liquid as well as in the vapor phase and activity coefficients in the liquid phase. For that purpose a static vapor−liquid equilibrium apparatus was used which allowed simultaneous measurement of the liquid and vapor compositions as well as the vapor saturation pressure of the reactive mixture in chemical equilibrium. From the results obtained in this work,[1] we have drawn the important conclusion that values of K_X in mixtures containing

Table 5. Thermodynamic Functions $\Delta_r H^\circ_m$ and $\Delta_r S^\circ_m$ of the (1-Alkoxyethyl)benzene Synthesis Reactions in the Liquid Phase at T = 298.15 K Obtained from log $K_X = a + b(1000T/\mathrm{K})^{-1}$ and Data of $\Delta_r H^\circ_m$ Obtained from Enthalpies of Formation of the Reaction Participants

alkyl	$\Delta_r H^\circ_{m(\mathrm{equilibrium})}$[a] (kJ·mol^{-1})	$\Delta_r H^\circ_{m(\mathrm{calorimetry})}$[b] (kJ·mol^{-1})	a	b	$\langle T\rangle^c$ (K)	$\Delta_r S^\circ_m$[a] (J·K^{-1}·mol^{-1})
methyl	−24.7 ± 1.2	−25.4 ± 2.4	−2.52 ± 0.007	1.29 ± 0.03	383.1	−48.2 ± 1.4
ethyl	−22.6 ± 0.6		−2.40 ± 0.003	1.18 ± 0.02	383.1	−45.9 ± 0.7
propyl	−23.2 ± 2.5		−2.36 ± 0.009	1.21 ± 0.07	383.1	−45.2 ± 2.5
butyl	−25.3 ± 2.1	−26.2 ± 3.1	−2.55 ± 0.008	1.32 ± 0.06	383.1	−48.8 ± 2.8

[a] Derived from the temperature dependence of K_X and referring to the average temperature of the equilibrium study. Corrections to the reference temperature 298.15 K are assumed to be negligible within the boundaries of the experimental errors (see text). [b] Calculated from the enthalpies of formation of the reaction participants. [c] The average temperature of the equilibrium study.

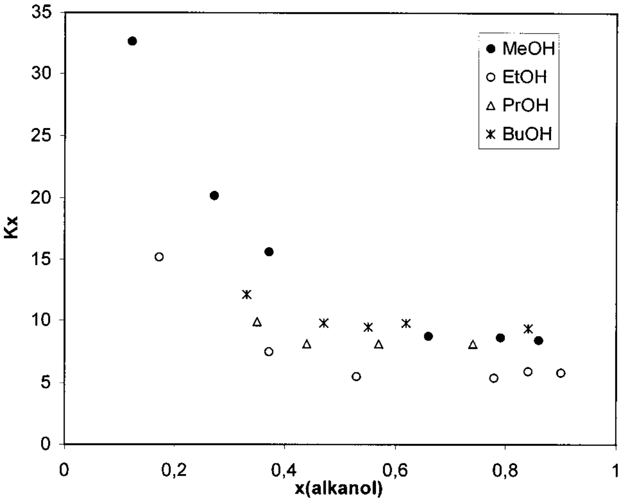

Figure 2. Equilibrium constants K_X for the (1-alkoxyethyl)benzene synthesis reaction as a function of the alkanol mole fraction x in the equilibrium mixture at T = 373.1 K.

an excess of methanol are indistinguishable from the thermodynamic constants K_a for the methyl cumyl ether synthesis reaction within the experimental error limits. The same conclusion was drawn from the investigation of chemical equilibria of reaction of other n-alkanols with α-methylstyrene.[2] Therefore, the assumption is allowed that the reaction enthalpy obtained from the temperature dependence of K_X measured above $x_{\mathrm{MeOH}} > 0.5$ provides the standard enthalpy of reaction $\Delta_r H^\circ_m$(l) as if it would have been obtained from K_a values.

Inspection of Tables 1−4 and Figure 2 shows that K_X values are almost independent of the mole fraction of alkanol if $x_{\mathrm{AlkOH}} > 0.5$. Only these values were used to derive the average value of K_X at each temperature of investigation. For all four systems studied, a plot of log K_X as a function of $1/T$ with K_X values obtained from the glass vials technique at values of $x_{\mathrm{AlkOH}} \geq 0.5$ gives straight lines which are almost parallel to each other (see Figure 3). Experimental values of K_X were approximated as a function of temperature by the linear equation log $K_X = a + b(T/\mathrm{K})^{-1}$ using the method of least squares.[17] The slopes of these lines give the standard enthalpy of reaction $\Delta_r H^\circ_m$ of the (1-alkoxyethyl)benzene synthesis reaction in the liquid state, and the intercept gives the standard entropy of reaction $\Delta_r S^\circ_m$. Numerical results are presented in Table 5.

The thermodynamic functions $\Delta_r H^\circ_m$ and $\Delta_r S^\circ_m$ refer to the average temperature of the equilibrium study. The temperature range of the equilibrium studies differs from the reference temperature by over 85 K. This fact inhibited the proper interpretation of the equilibrium data. From the available c_p data for alkanols, olefins, and ethers,[19] the change of the enthalpy of reactions, caused by extrapolation within 85 K has been assessed to be not larger than (1.5 to 2.5) kJ·mol^{-1}. Any corrections are negligible, taking into account the individual error bars of about (1.0 to 2.5) kJ·mol^{-1} typical of the equilibrium measurements. In further calculations it was assumed that the enthalpy of reaction hardly changes on passing from the average temperature of the experimental range to T = 298.15 K.

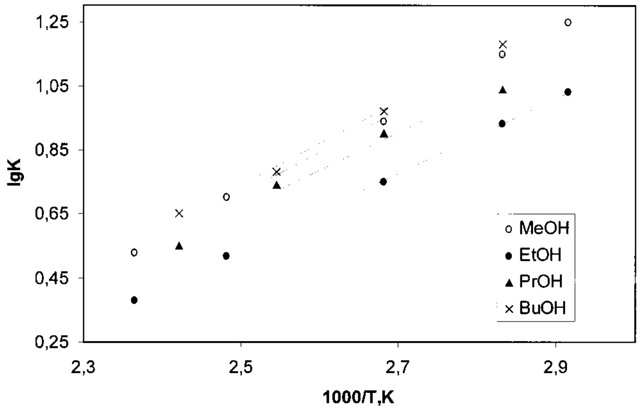

Figure 3. Equilibrium ratios K_X at a mole fraction $x_{\mathrm{alcohol}} > 0.5$ as a function of temperature (data points represent the average value of K_X at a mole fraction $x_{\mathrm{alcohol}} > 0.5$ at the appropriate temperature of investigation). Straight lines are according to log $K_X = a + b(T/\mathrm{K})^{-1}$ with a and b from Table 5.

Table 6. Results for a Typical Combustion Experiment at T = 298.15 K (p° = 0.1 MPa)[a]

	MeEB	BuEB
m (substance)/g[b]	0.318 88	0.326 02
m' (cotton)/g[b]	0.001 02	0.001 13
m'' (polythene)/g[b]	0.244 17	0.237 16
ΔT_c/K[c]	1.5212	1.5622
$\epsilon_{\mathrm{calor}}(-\Delta T_c)$/J	−23 267.66	−23 895.41
ΔU_{corr}/J[d]	10.30	10.35
$-m'\Delta_c u'$/J	17.28	19.15
$-m''\Delta_c u''$/J	11 319.96	10 994.98
$\Delta_c u^\circ$ (substance)/J·g^{-1}	−37 364.3	−39 462.4

[a] For the definition of the symbols, see ref 3; V_{bomb} = 0.3289 dm^3; p^i_{gas} = 3.04 MPa; m^i_{water} = 1.00 g; E_{ignition} = 5.4 J; m_{platin} = 9.64 g. [b] Masses obtained from apparent masses. [c] $\Delta T_c = T^f - T^i + \Delta T_{\mathrm{corr}}$. [d] ΔU_{corr}, the correction to the standard state is the sum of items 81−85, 87−90, 93, and 94 in Hubbard et al.[3]

3.2. Energies of Combustion and Enthalpies of Formation. The results for a typical combustion experiment of (1-alkoxyethyl)benzenes are given in Table 6. The individual values of the standard specific energies of combustion $\Delta_c u^\circ$ are given as follows (in J·g^{-1}): (1-methoxyethyl)benzene, −37 364.3, −37 375.1, −37 362.4, −37 360.0, and −37 361.6; (1-butoxyethyl)benzene, −39 462.4, −39 451.7, −39 460.8, −39 474.0, −39 461.9, and −39 453.7. The mean values of $\Delta_c u^\circ$ and their standard deviation from the mean

Table 7. Thermochemical Data of (1-Alkoxyethyl)benzenes at T = 298.15 K ($p°$ = 0.1 MPa)

	$\Delta_c u°(l)$ ($J \cdot g^{-1}$)	$\Delta_c H^o_m(l)$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^o_m(l)$ ($kJ \cdot mol^{-1}$)	$\Delta^g_l H^o_m$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^o_m(g)$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^o_m(g)(calc)^b$ ($kJ \cdot mol^{-1}$)	$H_S{}^c$ ($kJ \cdot mol^{-1}$)
MeEB	−37 364.7 ± 2.7	−5088.9 ± 1.9	−161.5 ± 2.2	49.08 ± 0.43	−112.4 ± 2.2	−116.9	4.5
EtEB	-	-	−196.2 ± 1.1[a]	52.63 ± 0.20	−143.6 ± 1.1	−149.9	6.3
PrEB	-	-	−222.3 ± 2.7[a]	56.71 ± 0.24	−165.6 ± 2.7	−171.0	5.4
BuEB	−39 460.7 ± 3.2	−7044.8 ± 2.6	−249.8 ± 3.0	59.80 ± 0.34	−190.0 ± 3.0	−192.5	2.5

[a] Calculated from the results of the chemical equilibrium study (see text). [b] Calculated as the sum of the strain-free increments (see text). [c] Strain enthalpy of ethylbenzene derivatives $H_S = \Delta_f H^o_m(g)(exp) - \Delta_f H^o_m(g)(calc)$.

Table 8. Vapor Pressure p and Molar Enthalpies of Vaporization $\Delta^g_l H^o_m$ of (1-Alkoxyethyl)benzenes Measured Using the Transpiration Method

T (K)[a]	m (mg)[b]	$V(N_2)$ (dm^3)[c]	p (Pa)[d]	T (K)[a]	m (mg)[b]	$V(N_2)$ (dm^3)[c]	p (Pa)[d]
(1-Methoxyethyl)benzene, $\ln(p/Pa) = (25.22 \pm 0.18) - (5919 \pm 52)(T/K)^{-1}$							
278.3	8.51	3.094	54.36	298.2	7.66	0.637	222.3
278.4	8.02	3.020	50.81	298.2	7.65	0.638	222.5
283.2	8.17	2.074	75.98	298.5	12.5	1.030	224.2
283.5	8.81	2.180	76.06	303.1	12.5	0.734	313.8
288.2	8.25	1.371	113.9	303.5	7.05	0.424	305.3
288.5	7.96	1.350	109.7	308.1	16.4	0.734	411.6
293.1	7.38	0.893	154.7	308.5	6.89	0.304	415.4
293.4	10.1	1.198	155.7	313.4	5.54	0.182	556.5
$\Delta^g_l H^o_m(\langle T \rangle = 295.8\ K) = (49.21 \pm 0.43)\ kJ \cdot mol^{-1}$; $\Delta^g_l H^o_m(298.15\ K) = (49.08 \pm 0.43)\ kJ \cdot mol^{-1}$							
(1-Ethoxyethyl)benzene, $\ln(p/Pa) = (25.91 \pm 0.08) - (6303 \pm 24)(T/K)^{-1}$							
286.3	6.08	2.082	49.13	301.0	8.09	0.942	142.5
288.3	11.1	3.222	57.62	303.5	7.57	0.744	168.7
290.2	6.59	1.686	65.35	306.2	7.35	0.595	204.6
291.4	9.29	2.157	71.94	309.2	7.57	0.496	252.5
294.3	9.77	1.785	91.17	312.2	7.37	0.397	307.4
297.4	9.24	1.363	112.8	315.2	6.67	0.298	370.8
298.4	7.98	1.116	118.9	318.2	8.07	0.298	448.1
$\Delta^g_l H^o_m(\langle T \rangle = 302.2\ K) = (52.41 \pm 0.20)\ kJ \cdot mol^{-1}$; $\Delta^g_l H^o_m(298.15\ K) = (52.63 \pm 0.20)\ kJ \cdot mol^{-1}$							
(1-Propoxyethyl)benzene, $\ln(p/Pa) = (26.54 \pm 0.10) - (6778 \pm 29)(T/K)^{-1}$							
287.8	2.67	2.100	19.46	303.6	4.20	0.950	66.92
288.8	4.64	3.249	21.79	306.6	4.27	0.750	86.12
289.8	2.53	1.700	22.73	309.6	4.13	0.600	104.1
291.8	3.88	2.175	27.19	312.6	4.22	0.500	127.5
294.7	4.06	1.800	34.27	315.5	4.13	0.400	156.0
297.7	3.97	1.375	43.82	318.5	3.78	0.300	190.2
300.7	4.04	1.125	54.44	321.5	4.60	0.300	231.7
$\Delta^g_l H^o_m(\langle T \rangle = 304.6\ K) = (56.36 \pm 0.24)\ kJ \cdot mol^{-1}$; $\Delta^g_l H^o_m(298.15\ K) = (56.71 \pm 0.24)\ kJ \cdot mol^{-1}$							
(1-Butoxyethyl)benzene, $\ln(p/Pa) = (26.90 \pm 0.14) - (7192 \pm 41)(T/K)^{-1}$							
278.2	0.460	2.552	2.902	298.1	0.615	0.590	15.85
282.8	0.846	2.947	4.275	302.8	1.06	0.655	23.65
283.2	0.371	1.340	4.469	303.2	0.829	0.543	24.22
287.8	0.772	1.746	6.570	307.8	1.28	0.548	33.91
288.2	0.432	1.021	6.676	308.2	1.39	0.622	35.51
292.8	0.922	1.350	10.05	312.8	1.61	0.473	49.04
293.1	0.512	0.766	10.32	317.8	1.56	0.323	69.51
297.8	1.23	1.129	15.92				
$\Delta^g_l H^o_m(\langle T \rangle = 298.0\ K) = (59.80 \pm 0.34)\ kJ \cdot mol^{-1}$; $\Delta^g_l H^o_m(298.15\ K) = (59.80 \pm 0.34)\ kJ \cdot mol^{-1}$							

[a] Temperature of saturation, N_2 gas flow 0.22−0.42 $cm^3 \cdot s^{-1}$. [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen used to transfer mass m of the sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at 243 K.

are presented in Table 7. Standard molar enthalpies of combustion $\Delta_c H^o_m$ and of formation $\Delta_f H^o_m$ (see Table 7) were calculated according to the established procedure[3] using the molar enthalpies of formation for $H_2O(l)$ and $CO_2(g)$ as recommended by CODATA.[5] The assigned standard deviations of the mean values of $\Delta_f H^o_m$ include[16] 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.

3.3. Enthalpies of Vaporization. Results obtained from measurements of the vapor pressure p of (1-alkoxyethyl)benzenes using the transpiration method are presented in Table 8. To ensure that vapor saturation is reached in the carrier gas at each specified temperature, the experiments were carried at two nitrogen flow rates, 0.22 and 0.42 $cm^3 \cdot s^{-1}$. No difference of the results was observed. Because of the slight deviations of the average temperatures of measurement from the reference temperature 298.15 K, the observed values of the enthalpy of vaporization had to be corrected to this reference temperature. The corrections were estimated with the help of the correction formula

$$\{\Delta^g_l H^o_m(\langle T \rangle) - \Delta^g_l H^o_m(298.15\ K)\}/kJ \cdot mol^{-1} = -5.44 \times 10^{-2}\{(\langle T \rangle/K) - 298.15\} \quad (5)$$

following the recommendation of Chickos et al.[6] where $\langle T \rangle$

is the temperature averaged over the temperature range covered by the experiments. With these corrections (the uncertainty of the correlation was not taken into account) and the measured values of $\Delta_l^g H_m^o(\langle T \rangle)$ and $(\langle T \rangle)$ from Table 8, the standard enthalpies of vaporization at T = 298.15 K were calculated (Tables 7 and 8).

4. Discussion

4.1. Comparison of the Reaction Enthalpies Obtained from Equilibrium Studies and from Combustion Experiments. We investigated the chemical equilibrium of reactions of the synthesis of (1-alkoxyethyl)benzenes from *n*-alkanols and styrene in the temperature range (343 to 423) K and derived the standard enthalpies of these reactions in the liquid phase. The validity of the results obtained from the chemical equilibrium study can be verified by comparison with the values of the reaction enthalpies calculated from the formation enthalpies of the reaction participants. For this purpose the standard molar enthalpy of formation $\Delta_f H_m^o(l)$ of (1-methoxyethyl)- and (1-butoxyethyl)benzenes at 298.15 K was measured by means of combustion calorimetry in this work (Table 7). Further experimental data necessary for comparison are available in the literature: for styrene[7] $\Delta_f H_m^o(l) = (103.4 \pm 0.9)$ kJ·mol^{-1}, for methanol[8,18] $\Delta_f H_m^o(l)$ $-(239.5 \pm 0.2)$ kJ·mol^{-1}, and for ethanol[8,18] $\Delta_f H_m^o(l) = -(277.0 \pm 0.3)$ kJ·mol^{-1}. Data for propanol, $\Delta_f H_m^o(l) = (-302.5 \pm 0.2)$ kJ·mol^{-1}, and for butanol, $\Delta_f H_m^o(l) = (-327.0 \pm 0.2)$ kJ·mol^{-1}, were taken from Mosselman and Dekker.[9,18] These data were used to calculate independently $\Delta_r H_{m(\text{calorimetry})}^o$ of the (1-alkoxyethyl)benzene synthesis reaction in the liquid phase [e.g., for (1-methoxyethyl)benzene]:

$$\Delta_r H_m^o(l)_{(\text{calorimetry})} = \Delta_f H_m^o(l)_{(\text{MeEB})} - \Delta_f H_m^o(l)_{(\text{MeOH})} - \Delta_f H_m^o(l)_{(\text{Styrene})} = -(25.4 \pm 2.4)\ \text{kJ·mol}^{-1}$$

The comparison with experimental values obtained from the chemical equilibrium study is given in Table 5. The calculated values of $\Delta_r H_m^o(l)_{(\text{calorimetry})}$ for the reactions of (methoxyethyl)- and (butoxyethyl)benzene are in very close agreement, being within the limits of the experimental uncertainties with those of $\Delta_r H_m^o(l)_{(\text{equilibrium})}$ derived from the chemical equilibrium studies.

The thermodynamic consistency observed allows one to calculate the enthalpy of formation of (1-ethoxyethyl)benzene, $\Delta_f H_m^o(l) = -(196.2 \pm 1.1)$ kJ·mol^{-1}, and of (1-propoxyethyl)benzene, $\Delta_f H_m^o(l) = -(222.3 \pm 2.7)$ kJ·mol^{-1}, from the known enthalpies of formation of alkanols and styrene and standard enthalpies of reaction obtained from the temperature dependence of K_X (see Table 7).

4.2. Strain Enthalpies H_S of (1-Alkoxyethyl)benzenes. An important test to establish the validity of the experimental and calculation procedures presented in this paper provides the comparison of strain enthalpies of (1-alkoxyethyl)benzenes, which could be derived from their gaseous standard molar enthalpies of formation $\Delta_f H_m^o(g)$ at 298.15 K (Table 7). Indeed, the (methoxyethyl)-, (ethoxyethyl)-, (propoxyethyl)-, and (butoxyethyl)benzenes listed in Table 7 present a typical example of the homologue series. It is well established that for such series as alkanes or alkanols[9] the enthalpic contribution into $\Delta_f H_m^o(g)$ from the CH_2 group should remain constant. In other words, no additional strain interactions in a molecule are expected by passing from (methoxyethyl)- to (butoxyethyl)benzene. The resulting values of $\Delta_f H_m^o(g)$ of (1-alkoxyethyl)benzenes calculated as the sum of $\Delta_f H_m^o(l)$ and $\Delta_l^g H_m^o$ are shown in Table 7.

We define the strain enthalpy H_S of a molecule as the difference between the experimental standard enthalpy of formation $\Delta_f H_m^o(g)$ and the calculated sum of the strain-free Benson-type increments[10] for this molecule. The strain-free increments for the calculation of enthalpies of formation of alkanes,[11] alkylbenzenes,[12] and ethers[13,14] are already well established. By using these group additivity parameters and the values of $\Delta_f H_m^o(g)$ of ethylbenzene derivatives (Table 7), their values of strain enthalpies $H_S = \{\Delta_f H_m^o(g) - \sum\text{increments}\}$ have been estimated (Table 7).

All (1-alkoxyethyl)benzenes studied here are very similarly strained by about 5 kJ·mol^{-1} (Table 7). This fact is a further indication that the data for $\Delta_f H_m^o(g)$ of (1-alkoxyethyl)benzenes, obtained by combining the different experimental techniques (calorimetry, transpiration, and equilibrium study), are generally consistent, supporting the confidence in the experimental procedures used. What reasons cause strain in these molecules? Elucidation of the nature of the strain in (1-alkoxyethyl)benzenes is aided by comparison with the strain of the similarly shaped isopropylbenzene:[15] $\Delta_f H_m^o(g) = -(3.9 \pm 1.1)$ kJ·mol^{-1} and strain enthalpy $H_S = 5.0$ kJ·mol^{-1}. Isopropylbenzene is a relevant structural pattern of strain in the (1-alkoxyethyl)benzenes studied. Its strain enthalpy is a reflection of the intrinsic strain of the molecule due to steric repulsions of methyl groups and the benzene ring attached to the central tertiary carbon atom. It is expected from analogy with the strain of isopropylbenzene that the observed amount of destabilization in (alkoxyethyl)benzene derivatives could most likely be attributed to the steric repulsions of methyl groups and the benzene ring attached to the central tertiary carbon atom. Therefore, it can be concluded that no additional group additivity parameters or correction terms are necessary (besides those of the correction for H_S = 5.0 kJ·mol^{-1} like in isopropylbenzene) for the group contribution correlation for $\Delta_f H_m^o(g)$ of (1-alkoxyethyl)benzenes.

Literature Cited

(1) Heintz, A.; Verevkin, S. P. Simultaneous study of chemical and vapor−liquid equilibria in the reacting system of the methyl cumyl ether synthesis from methanol and α-methyl-styrene. *Fluid Phase Equilib.* **2001**, *179* (1−2), 85−100.

(2) Verevkin, S. P.; Heintz, A. Chemical equilibria study in the reacting system of the alkyl cumyl ether synthesis from *n*-alkanols and α-methyl-styrene. *J. Chem. Eng. Data* **2001**, *46*, 41−46.

(3) Hubbard, W. N.; Scott, D. W.; Waddington, G. In *Experimental Thermochemistry*; Rossini, F. D., Ed.; Interscience: New York, 1956; pp 75−127.

(4) Atomic weights of the elements. *Pure Appl. Chem.* **1994**, *66*, 2423−2444.

(5) *CODATA Key Values for Thermodynamics*; Cox, J. D., Wagman, D. D., Medvedev, V. A., Eds.; Hemisphere: New York, 1989.

(6) Chickos, J. S.; Hosseini, S.; Hesse, D. G.; Liebman, J. F. Heat Capacity Corrections to a Standard State: A Comparison of New and Some Literature Methods for Organic Liquids and Solids. *Struct. Chem.* **1993**, *4*, 271−278.

(7) Prosen, E. J.; Rossini, F. D. Heats of formation and combustion of 1,3-butadiene and styrene. *J. Res. NBS* **1945**, *34*, 59−63.

(8) Chao, J.; Rossini, F. D. Heats of combustion, formation, and isomerization of nineteen alkanols, *J. Chem. Eng. Data* **1965**, *10*, 374−379.

(9) Mosselman, C.; Dekker, H. Enthalpies of formation of *n*-alkan-1-ols. *J. Chem. Soc., Faraday Trans. 1* **1975**, 417−424.

(10) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976; p 274.

(11) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. B. The evaluation of strain in hydrocarbons. The strain in adamantane and its origin. *J. Am. Chem. Soc.* **1970**, *92*, 2377−2386.

(12) Beckhaus, H.-D. Force Field for the Calculation of Structure and Enthalpy of Formation of Alkylbenzenes. *Chem. Ber.* **1983**, *116*, 86−96.
(13) Rakus, K.; Verevkin, S. P.; Peng, W.-H.; Beckhaus, H.-D.; Rüchardt, C. Geminal Substituent Effects. 11. The Anomeric Effect in Ortho esters. The Concept of Geminal Pairwise Interactions for the Interpretation of Enthalpies of Formation. *Liebigs Ann.* **1995**, 2059−2067.
(14) Verevkin, S. P.; Beckhaus, H.-D.; Beleńkaja, R. S.; Rakus, K.; Rüchardt, C. Geminal Substituent Effects. 9. Enthalpies of Formation and Strain Free Increments of Branched Esters and Ethers. *Thermochim. Acta* **1996**, *279*, 47−64.
(15) Prosen, E. J.; Gilmont, R.; Rossini, F. D. Heats of combustion of benzene, toluene, ethyl-benzene, *o*-xylene, *m*-xylene, *p*-xylene, *n*-propylbenzene, and styrene. *J. Res. NBS* **1945**, *34*, 65−70.
(16) Olofsson, G. *Combustion Calorimetry*; Sunner, S., Mansson, M., Eds.; Pergamon: Oxford, 1979.
(17) *Thermochemistry and Equilibria of Organic Compounds*; Frenkel, M., Ed.; VCH Publishers Inc.: New York, 1993.
(18) Pedley, J. P.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.
(19) Lide, D. R.; Kehiaian, H. V. *CRC Handbook of Thermophysical and Thermochemical Data*; CRC Press: Boca Raton, FL, 1994.

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