

# Chemical Equilibria Study of the Reacting System of the Alkyl Cumyl Ether Synthesis from *n*-Alkanols and $\alpha$ -Methylstyrene

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The chemical equilibrium of the reactive systems *n*-alkanol +  $\alpha$ -methylstyrene  $\rightleftharpoons$  alkyl cumyl ether (alkyl is ethyl, propyl, and butyl) was studied in the liquid phase in the temperature range (300 to 383) K using a cation exchanger as heterogeneous catalyst. Equilibrium ratios  $K_x$  obtained from concentrations of the reaction participants in the mixtures with an excess amount of alkanol are practically independent of the reactive mixture composition and can be identified with the thermodynamic equilibrium constant  $K_a$ . Enthalpies of reactions  $\Delta_r H_m^0$  of alkyl cumyl ether synthesis in the liquid phase were obtained from the temperature dependence of  $K_a$  and showed a good agreement with those reaction enthalpies derived from the values  $\Delta_r H_m^0(l)$  of the reactions participants measured for alkyl cumyl ethers by combustion calorimetry. The standard molar enthalpies of vaporization of alkyl cumyl ethers were obtained from the temperature dependence of the vapor pressure measured by using the transpiration method. Resulting values of  $\Delta_r H_m^0(g)$  were used to prove the consistency of the experimental data and to derive strain enthalpies of alkyl cumyl ethers. The strain effects were discussed in terms of deviations of  $\Delta_r H_m^0(g)$  from the group additivity rules.

## 1. Introduction

The use of oxygenates based on ethers such as methyl *tert*-butyl ether (MTBE) and *tert*-amyl methyl ether (TAME) has seen tremendous growth in the 1990s. These ethers have been the oxygenates of choice, mainly due to the economics and availability of feedstocks. However, over the last years there has been a growing concern about contamination of a groundwater by MTBE, due to leaking storage tanks and pipelines. The major factor affecting the impact of MTBE on potable water stems from its high water solubility. Therefore, seeking alternative additives remains an important problem. Beside the widely used MTBE and TAME, further candidates are alkyl cumyl ethers synthesized in the liquid phase over acid-functionalized ion-exchanged resin catalysts from *n*-alkanols and  $\alpha$ -methylstyrene (see Figure 1).

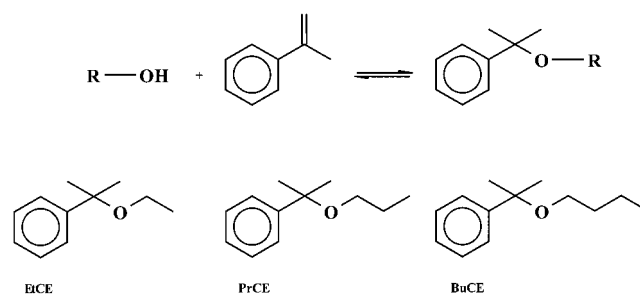
It has been well documented in the literature that the reacting systems of the alkyl ether syntheses such as those of MTBE<sup>1</sup> and TAME<sup>2</sup> behave strongly nonideally. We have established recently<sup>3</sup> that the methyl cumyl ether synthesis mixture also deviates distinctly from ideal behavior. It has been observed that the equilibrium ratio  $K_x$ , defined as

$$K_x = \frac{x_{\text{ether}}}{x_{\text{alkanol}} x_{\alpha\text{-MS}}} \quad (1)$$

strongly depends on the composition of the equilibrium mixture;  $x_i$  in eq 1 are the mole fractions of reaction participants in the liquid phase. The thermodynamic equilibrium constant  $K_a$  in the liquid phase is related to  $K_x$  by the following equation:

$$K_a = \frac{\gamma_{\text{ether}}}{\gamma_{\text{alkanol}} \gamma_{\alpha\text{-MS}}} K_x \quad (2)$$

where  $\gamma_i$  is the activity coefficient of component *i* depending on the mixture composition. In our previous work<sup>3</sup> we investigated the chemical equilibrium in the liquid and gaseous phases 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 the 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 being in chemical equilibrium. From the results obtained in this work<sup>3</sup> we have drawn the important conclusion that values of  $K_x$  in excess methanol are indistinguishable from the thermodynamic constants  $K_a$  for the methyl cumyl ether synthesis reaction within the experimental error limits. Therefore, the assumption is allowed that the reaction enthalpy obtained from the temperature dependence of  $K_x$  measured above  $x_{\text{MeOH}} > 0.5$



**Figure 1.** Reaction of the alkyl cumyl ether synthesis (R = methyl, ethyl, propyl, and butyl) and ethers studied in this work: ethyl cumyl ether (EtCE); propyl cumyl ether (PrCE); butyl cumyl ether (BuCE).

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provides the standard enthalpy of reaction  $\Delta_r H_m^\circ(l)$  as if it would have been obtained from  $K_a$  values. It is of interest to know whether such an assumption could be generalized for all ether synthesis reactions. Thus, as an extension of our previous work we have performed further systematic investigation of the chemical equilibrium in the reacting systems of the alkyl cumyl ether synthesis such as ethyl cumyl ether (EtCE), propyl cumyl ether (PrCE), and butyl cumyl ether (BuCE) (see Figure 1). We report new experimental data of the reaction enthalpies 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 data on  $\Delta_r H_m^\circ(l)$  are compared with those calculated from differences of the enthalpies of formation of the reaction participants. For the latter purpose, standard molar enthalpies of formation in the liquid phase  $\Delta_f H_m^\circ(l)$  of ethyl cumyl ether and butyl cumyl ether were additionally obtained from calorimetrically measured enthalpies of combustion. Further support of the reliability of the procedures applied in this work is expected from quantitative analysis of standard molar enthalpies of formation in the gaseous phase  $\Delta_f H_m^\circ(g)$ . Values of  $\Delta_f H_m^\circ(g)$  of alkyl cumyl ethers were obtained from calorimetrically measured  $\Delta_f H_m^\circ(l)$  and their enthalpies of vaporization measured by a transpiration method. Thus, the systematic investigation of the alkyl cumyl ethers synthesis reactions would be of value for three reasons. First, if good agreement with the standard reaction enthalpies,  $\Delta_r H_m^\circ(l)$ , obtained from the temperature dependence of  $K_x$  is found, it would confirm that the reliability and accuracy of our procedures are satisfactory. Second, it would allow us to establish the guideline of the thermodynamic treatment of the equilibrium constants in the strongly nonideal reactive systems. Third, experimental values of  $\Delta_f H_m^\circ(g)$  would provide useful information on the strain effects and the relation between structure and properties of alkyl cumyl ethers. The results of the study also could be aimed at an improvement of the Benson<sup>4</sup> group-contribution methodology.

## 2. Experimental Section

**2.1. Materials.**  $\alpha$ -Methylstyrene ( $\alpha$ -MS), ethanol (EtOH), propan-1-ol (PrOH), and butan-1-ol (BuOH) (water content less than 0.01%) were purchased from Merck. GC analyses of the as-purchased samples gave a purity > 99.9% in agreement with specifications. Alkyl cumyl ethers (Figure 1) were synthesized via alkylation of an appropriate *n*-alkanol with  $\alpha$ -methylstyrene in the presence of a catalytic amount of cation-exchange resin in  $H^+$  form (Amberlist 15, Aldrich) at room temperature. Prior to the experiments the cation-exchange resin Amberlist 15 in  $H^+$  form was dried for 8 h at 383 K in a vacuum oven at reduced pressure.

The pure samples of alkyl cumyl ethers were obtained by repeated distillations using a spinning-band column at reduced pressure under  $N_2$ , after being dried with molecular sieves (0.4 nm). No impurities could be detected in ethyl and butyl cumyl ethers by GC. In the sample of propyl cumyl ether about 0.8% of nonidentified components has been found by GC. Repeated distillations did not improve the quality of the specimen. Thus, the sample of propyl cumyl ether with the purity 99.2% satisfies only the requirements for the determination of vaporization enthalpies but not the requirements needed in the combustion experiments. As a consequence no combustion experiments were performed with propyl cumyl ether, and the enthalpy of formation  $\Delta_f H_m^\circ(l)$  for this compound was obtained only

from the results of the equilibrium study of the reaction of its synthesis.

**2.2. Chemical Equilibrium Study.** Glass vials with screwed caps were filled two-thirds full with the initial liquid mixture of alkanol and  $\alpha$ -methylstyrene. The cation-exchange resin Amberlist 15 (Aldrich) in  $H^+$  form was added as a solid catalyst. The quantity of catalyst was approximately 10% from the weight of the mixture. The vial was thermostated at  $T_i \pm 0.1$  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. The thermostating of 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 analyzed with a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was  $12.1 \text{ cm}^3 \cdot \text{s}^{-1}$ . 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  $0.25 \text{ }\mu\text{m}$ . The standard temperature program of the GC was  $T = 353 \text{ K}$  for 180 s followed by a heating rate of  $0.167 \text{ K} \cdot \text{s}^{-1}$  to  $T = 523 \text{ K}$ . Response factors of all reagents were determined using calibration mixtures of the corresponding components prepared gravimetrically.

**2.3. Combustion Calorimetry.** For measurements of the energies of combustion of the alkyl cumyl ethers, an isoperibolic calorimeter<sup>5</sup> equipped with a static bomb and an isothermal water jacket was used. The temperature in the water jacket was maintained within  $\pm 0.0015 \text{ K}$  with the help of 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 polyethylene ampules (Fa. NeoLab, Heidelberg) of  $1 \text{ cm}^3$  volume as the sample container for liquids in order to reduce the capillary effect and make the encapsulation easier. The liquid sample was transferred to a polyethylene ampule with a syringe. The narrow neck of the container was compressed with special tweezers and sealed by heating with hot air. Then, the loaded container was placed in the platinum crucible within the bomb, knotted to the wire, and burned in oxygen at a pressure of 3.04 MPa with 1.00 g of water added to the bomb. The ignition was performed by a capacitor discharged through a platinum wire. The ignition of the sample and the recording of the temperature rise were performed automatically using an interface connection to a computer. Thermometric measurements were carried out using  $100 \text{ }\Omega$  Pt-resistance thermometers by recording the amplified signal with a digital voltmeter. The initial temperature of the combustion experiments was 298.15 K for each experiment. The corrected temperature rise was calculated using recommendations from the literature.<sup>6</sup> The energy equivalent of the calorimeters  $\epsilon_{\text{calor}}$  was determined with a standard reference sample of benzoic acid (sample SRM 39i, N.I.S.T.). From seven experiments,  $\epsilon_{\text{calor}}$  was measured to be  $15\,296.0 \pm 2.3 \text{ J} \cdot \text{K}^{-1}$ . The internal volume of the bomb was  $328.9 \text{ cm}^3$ . Nitrogen oxides were not formed in the calibration experiments due to the high purity of the oxygen used and preliminary bomb flushing. For converting the energy of the actual bomb

**Table 1. Experimentally Determined Composition of Equilibrium Mixtures and  $K_x$  Values in the Liquid Phase, Calculated from Eq 1, for the System Ethanol +  $\alpha$ -Methylstyrene  $\rightleftharpoons$  Ethyl Cumyl Ether<sup>a</sup>**

T/K	n	$x_{\text{EtOH}}$	$x_{\alpha\text{-MS}}$	$x_{\text{EtCE}}$	$K_x^b$
300.1	10	0.2984	0.2432	0.4563	$6.24 \pm 0.33$
	11	0.6243	0.1274	0.2483	$3.12 \pm 0.12$
	10	0.7710	0.0722	0.1568	$2.82 \pm 0.15$
	9	0.8192	0.0541	0.1267	$2.86 \pm 0.13$
	12	0.8478	0.0440	0.1082	$2.90 \pm 0.17$
303.1	14	0.2692	0.3142	0.4167	$4.93 \pm 0.28$
	16	0.5376	0.1883	0.2741	$2.71 \pm 0.09$
	11	0.7658	0.0801	0.1541	$2.51 \pm 0.11$
333.1	12	0.8146	0.0591	0.1262	$2.62 \pm 0.12$
	8	0.2280	0.5307	0.2413	$1.99 \pm 0.16$
	9	0.3783	0.3935	0.2282	$1.53 \pm 0.09$
	10	0.5948	0.2596	0.1456	$0.94 \pm 0.07$
	9	0.7641	0.1346	0.1013	$0.98 \pm 0.06$
353.1	10	0.8409	0.0853	0.0738	$1.03 \pm 0.05$
	11	0.4485	0.3728	0.1787	$1.07 \pm 0.08$
	9	0.6417	0.2309	0.1273	$0.86 \pm 0.07$
	12	0.7572	0.1671	0.0757	$0.60 \pm 0.04$
	11	0.8550	0.0963	0.0487	$0.59 \pm 0.05$
373.1	8	0.4775	0.4398	0.0827	$0.39 \pm 0.02$
	9	0.5884	0.3306	0.0810	$0.42 \pm 0.03$
	11	0.7100	0.2211	0.0689	$0.44 \pm 0.02$
	10	0.7716	0.1730	0.0554	$0.41 \pm 0.03$
	13	0.8633	0.1012	0.0355	$0.41 \pm 0.03$
393.1	11	0.5961	0.3469	0.0570	$0.27 \pm 0.02$
	10	0.7354	0.2208	0.0438	$0.27 \pm 0.03$
	11	0.8446	0.1252	0.0302	$0.29 \pm 0.03$

<sup>a</sup>  $T$  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. <sup>b</sup> Uncertainty is the standard deviation.

process to that of the isothermal process and reducing to standard states, the conventional procedure<sup>7</sup> was applied. The sample masses of alkyl cumyl ethers were reduced in vacuum, taking into consideration the density value  $\rho_{(293)} = 0.921 \text{ g}\cdot\text{cm}^{-3}$  for ethyl cumyl ether and  $\rho_{(293)} = 0.912 \text{ g}\cdot\text{cm}^{-3}$  for butyl cumyl ether, which were determined in a calibrated 10 cm<sup>3</sup> pycnometer. The energies of combustion of cotton thread,  $\Delta_c u^\circ(\text{CH}_{1.774}\text{O}_{0.887}) = -(16945.2 \pm 4.2) \text{ J}\cdot\text{g}^{-1}$ , and polyethene,  $\Delta_c u^\circ(\text{CH}_{1.930}) = -46361.0 \pm 3.1 \text{ J}\cdot\text{g}^{-1}$ , were measured earlier. The molar masses of alkyl cumyl ethers were evaluated from the relative atomic masses of the elements.<sup>8</sup>

**2.4. Transpiration Method.** The enthalpies of vaporization of alkyl cumyl ethers were determined using the method of transpiration in a saturated N<sub>2</sub> stream and applying the Clausius–Clapeyron equation. The method has been described before<sup>9</sup> and has proven to give results in excellent agreement with those of other established techniques for determining vapor pressures of pure substances in the range 0.005 to ~10 000 Pa and enthalpies of vaporization from the temperature dependence of the vapor pressure.

### 3. Results

**3.1. Equilibrium Constants and Reaction Enthalpies.** The experimental results of the chemical equilibrium study of the alkyl cumyl ethers' synthesis are listed in Tables 1–3. Inspection of these Tables and Figure 2 shows that  $K_x$  values are almost independent of the mole fraction of alkanol if  $x_{\text{AlkOH}} > 0.5$ . The same behavior has already been observed for the methyl cumyl ether synthesis reaction<sup>3</sup> also presented in Figure 2. For this system it has been shown that  $K_x \approx K_a$  for  $x_{\text{MeOH}} > 0.5$ . Therefore, the assumption is justified that the enthalpy of reaction obtained from the temperature dependence of  $K_x$  measured above  $x_{\text{AlkOH}} > 0.5$  provides the standard enthalpy of

**Table 2. Experimentally Determined Composition of Equilibrium Mixtures and  $K_x$  Values in the Liquid Phase, Calculated from Eq 1, for the System Propanol +  $\alpha$ -Methylstyrene  $\rightleftharpoons$  Propyl Cumyl Ether<sup>a</sup>**

T/K	n	$x_{\text{PrOH}}$	$x_{\alpha\text{-MS}}$	$x_{\text{PrCE}}$	$K_x^b$
300.1	10	0.0935	0.3711	0.5354	$15.43 \pm 0.36$
	11	0.1898	0.3210	0.4892	$8.03 \pm 0.25$
	13	0.2870	0.2584	0.4546	$6.13 \pm 0.11$
	10	0.6054	0.1351	0.2595	$3.17 \pm 0.18$
	11	0.7466	0.0724	0.1809	$3.35 \pm 0.18$
	8	0.8446	0.0399	0.1155	$3.43 \pm 0.11$
	12	0.9040	0.0234	0.0726	$3.43 \pm 0.12$
	9	0.3244	0.3739	0.3017	$2.49 \pm 0.08$
	11	0.5848	0.2027	0.2124	$1.79 \pm 0.06$
	16	0.6022	0.1935	0.2043	$1.75 \pm 0.04$
343.1	10	0.4269	0.3524	0.2207	$1.47 \pm 0.05$
	9	0.5211	0.3247	0.1542	$0.91 \pm 0.03$
	15	0.6315	0.2392	0.1293	$0.86 \pm 0.05$
363.1	14	0.6654	0.1994	0.1352	$1.02 \pm 0.02$
	12	0.4801	0.4068	0.1131	$0.58 \pm 0.04$
	11	0.5694	0.3272	0.1034	$0.55 \pm 0.05$
383.1	7	0.6883	0.2210	0.0906	$0.60 \pm 0.02$
	13	0.7198	0.1955	0.0846	$0.60 \pm 0.05$
	12	0.5417	0.3734	0.0849	$0.42 \pm 0.04$
	10	0.6382	0.2860	0.0758	$0.41 \pm 0.04$
	10	0.6945	0.2371	0.0684	$0.42 \pm 0.05$
11	0.7795	0.1647	0.0558	$0.43 \pm 0.02$	

<sup>a</sup>  $T$  is the temperature of the investigation;  $n$  is the number of determinations of the composition within the time of the equilibrium study;  $x_i$  is the mole fraction measured chromatographically. <sup>b</sup> Uncertainty is the standard deviation.

**Table 3. Experimentally Determined Composition of Equilibrium Mixtures and  $K_x$  Values in the Liquid Phase, Calculated from the Eq 1, for the System Butanol +  $\alpha$ -Methylstyrene  $\rightleftharpoons$  Butyl Cumyl Ether<sup>a</sup>**

T/K	n	$x_{\text{BuOH}}$	$x_{\alpha\text{-MS}}$	$x_{\text{BuCE}}$	$K_x^b$
300.1	15	0.1102	0.4412	0.4486	$9.23 \pm 0.33$
	12	0.2804	0.3457	0.3739	$3.86 \pm 0.11$
	13	0.4025	0.2709	0.3266	$3.00 \pm 0.09$
	12	0.5121	0.1847	0.3021	$3.19 \pm 0.15$
	12	0.6029	0.1400	0.2571	$3.05 \pm 0.08$
	11	0.6281	0.1297	0.2422	$2.97 \pm 0.15$
	10	0.7411	0.0813	0.1746	$2.94 \pm 0.07$
	11	0.8266	0.0483	0.1241	$3.10 \pm 0.05$
	10	0.8886	0.0297	0.0817	$3.10 \pm 0.06$
	323.1	16	0.5872	0.2271	0.1857
343.1	11	0.7678	0.1122	0.1200	$1.39 \pm 0.07$
	12	0.8554	0.0661	0.0785	$1.39 \pm 0.06$
	11	0.4727	0.3780	0.1493	$0.84 \pm 0.05$
	12	0.6322	0.2345	0.1333	$0.90 \pm 0.06$
	13	0.7201	0.1650	0.1149	$0.97 \pm 0.04$
363.1	14	0.8160	0.1073	0.0767	$0.88 \pm 0.09$
	12	0.8514	0.0843	0.0643	$0.90 \pm 0.07$
	11	0.8908	0.0612	0.0480	$0.88 \pm 0.03$
	13	0.9246	0.0431	0.0323	$0.81 \pm 0.04$
	12	0.5131	0.3735	0.1134	$0.59 \pm 0.03$
	11	0.6062	0.2864	0.1075	$0.62 \pm 0.02$
	15	0.6870	0.2172	0.0959	$0.64 \pm 0.01$
383.1	16	0.7610	0.1640	0.0750	$0.60 \pm 0.03$
	11	0.8748	0.0822	0.0430	$0.60 \pm 0.01$
	10	0.6417	0.2918	0.0665	$0.36 \pm 0.05$
	9	0.7343	0.2144	0.0514	$0.33 \pm 0.03$
	11	0.8069	0.1485	0.0446	$0.37 \pm 0.06$
	12	0.8922	0.0846	0.0232	$0.31 \pm 0.03$

<sup>a</sup>  $T$  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. <sup>b</sup> Uncertainty is the standard deviation.

reaction  $\Delta_r H_m^\circ(\text{l})$ . For all three systems studied, a plot of  $\lg K_x$  as a function of  $1/T$  with  $K_x$  values obtained from the glass vials technique at values of  $x_{\text{AlkOH}}$  between 0.6 and 0.8 gives straight lines which are almost parallel to those of the methyl cumyl ether synthesis (see Figure 3). Experimental values of  $K_x$  were approximated as a function of temperature by the linear equation  $\lg K_x = a + b(T/\text{K})^{-1}$

**Table 4. Comparison of the Thermodynamic Functions  $\Delta_r H_m^F$  and  $\Delta_r S_m^S$  of the Alkyl Cumyl Ether Synthesis Reactions in the Liquid Phase at  $T = 298.15$  K;  $\lg K_x = a + b(1000/TK)^{-1}$** 

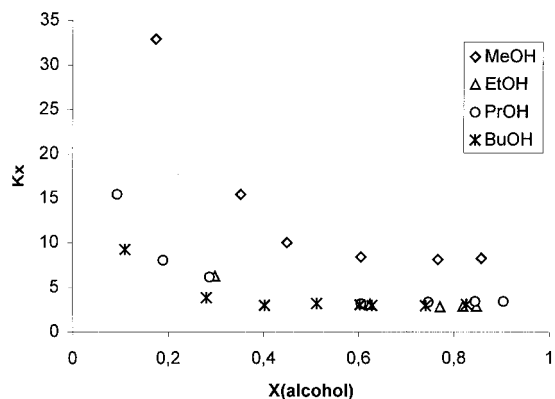
alkyl group	$\Delta_r H_m^F(\text{equilibrium})^a$	$\Delta_r H_m^F(\text{calorimetry})^b$	$a$	$b$	$\langle T \rangle^c$	$\Delta_r S_m^S^a$
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$			K	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
methyl	$-22.2 \pm 0.5^d$	$-24.0 \pm 2.6^d$	$-2.961 \pm 0.003^d$	$1.16 \pm 0.01^d$	$357.1^d$	$-56.7 \pm 0.3^d$
ethyl	$-24.9 \pm 1.2$	$-24.0 \pm 2.7$	$-3.88 \pm 0.01$	$1.30 \pm 0.03$	346.6	$-74.3 \pm 1.4$
propyl	$-24.5 \pm 1.6$		$-3.72 \pm 0.01$	$1.28 \pm 0.04$	341.6	$-71.2 \pm 2.0$
butyl	$-24.1 \pm 2.3$	$-25.1 \pm 2.8$	$-3.74 \pm 0.01$	$1.26 \pm 0.06$	341.6	$-71.6 \pm 3.0$

<sup>a</sup> Derived from the temperature dependence of  $K_x$  (it was assumed<sup>21</sup> that the enthalpy of reaction changes on passing from the average temperature of the experimental range to  $T = 298.15$  K are negligible within the boundaries of the uncertainties); uncertainty is the standard deviation. <sup>b</sup> Calculated from the enthalpies of formation of the reaction participants, measured by combustion calorimetry. <sup>c</sup> The average temperature of the equilibrium study. <sup>d</sup> Taken from our previous work.<sup>3</sup>

**Table 5. Results for a Typical Combustion Experiment at  $T = 298.15$  K ( $p^\circ = 0.1$  MPa)<sup>a</sup>**

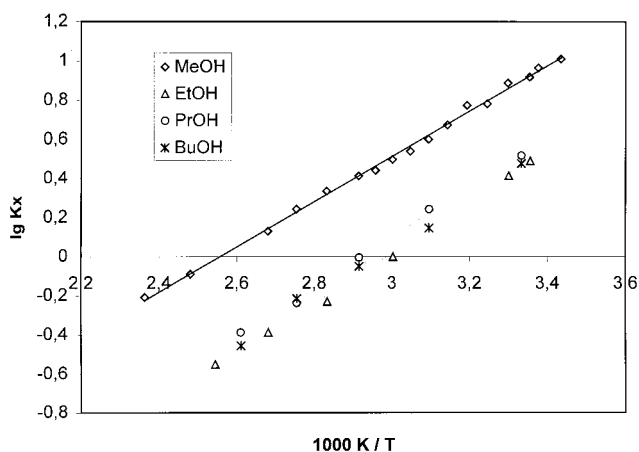
	ethyl cumyl ether	butyl cumyl ether
$m$ (substance) <sup>b/g</sup>	0.303 49	0.311 28
$m'$ (cotton) <sup>b/g</sup>	0.000 96	0.001 11
$m''$ (polythen) <sup>b/g</sup>	0.231 12	0.229 64
$\Delta T_c^c/\text{K}$	1.472 85	1.511 09
$(\epsilon_{\text{calor}})(-\Delta T_c)/\text{J}$	-22 528.71	-23 113.6
$\Delta U_{\text{corr}}^d/\text{J}$	10.40	10.61
$-m'\Delta_c u'/\text{J}$	16.27	18.81
$-m''\Delta_c u''/\text{J}$	10 714.95	10 646.33
$\Delta_c u^\circ$ (substance)/(J·g <sup>-1</sup> )	-38 820.5	-39 939.6

<sup>a</sup> For the definition of the symbols see ref 7:  $V_{\text{bomb}} = 0.3289$  dm<sup>3</sup>;  $p_{\text{gas}}^i = 3.04$  MPa;  $m_{\text{water}}^i = 1.00$  g;  $E_{\text{ignition}} = 5.4$  J;  $m_{\text{platin}} = 9.64$  g. <sup>b</sup> Masses obtained from apparent masses. <sup>c</sup>  $\Delta T_c = T' - T + \Delta T_{\text{corr}}$ . <sup>d</sup>  $\Delta U_{\text{corr}}$ , the correction to standard state, is the sum of items 81 to 85, 87 to 90, 93, and 94 in Hubbard et al.<sup>7</sup>

**Figure 2.** Concentration equilibrium constants  $K_x$  for the alkyl cumyl ether synthesis reaction as a function of alkanol mole fraction  $x$  in the equilibrium mixture at  $T = 300.1$  K.

using the method of least squares. The slopes of these lines when multiplied by the gas constant afford the standard enthalpy of reaction  $\Delta_r H_m^F$  of the alkyl cumyl ether synthesis reaction in the liquid or gaseous phase, and the intercept gives the standard entropy of reaction  $\Delta_r S_m^S$ . Numerical results are presented in Table 4. The errors in the thermodynamic functions from the equilibrium study are given by the standard deviations for the meaningful level 0.05.

**3.2. Energies of Combustion and Enthalpies of Formation.** The results for a typical combustion experiment of alkyl cumyl ethers are given in Table 5. The individual values of the standard specific energies of combustion,  $\Delta_c u^\circ$ , are given as follows (in J·g<sup>-1</sup>): ethyl cumyl ether 38 823.7, 38 820.5, 38 820.1, 38 824.3, 38 817.6, and 38 822.6; butyl cumyl ether: 39 941.0, 39 940.1, 39 939.6, 39 938.1, 39 937.5, and 39 939.8. The mean values of  $\Delta_c u^\circ$  and their standard deviations are presented in Table 6. Standard enthalpies of combustion  $\Delta_c H_m^F$  and enthalpies of formation  $\Delta_f H_m^F$  (see Table 6) were calcu-

**Figure 3.** Concentration equilibrium constants  $K_x$  at a mole fraction  $x_{\text{alcohol}}$  between 0.6 and 0.8 as a function of temperature.

lated according to the established procedure<sup>7</sup> using the molar enthalpies of formation for  $\text{H}_2\text{O}(\text{l})$  and  $\text{CO}_2(\text{g})$  as recommended by the IUPAC.<sup>10</sup> The assigned standard deviations of the mean values of  $\Delta_f H_m^F$  include the uncertainties from calibration, from the combustion energies of the auxiliary materials, and from the enthalpies of formation of the reaction products  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

**3.3. Enthalpies of Vaporization.** Results obtained from measurements of the vapor pressure  $p$  of alkyl cumyl ethers by the transpiration method are presented in Table 7. To ensure that vapor saturation is reached in the carrier gas at each specified temperature, the experiments were carried out at two nitrogen flow rates, 0.22 and 0.42 cm<sup>3</sup>·s<sup>-1</sup>. No difference of the results was observed. The results were treated together and are presented in Table 7. 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:

$$\{\Delta_f^g H_m^F(\langle T \rangle) - \Delta_f^g H_m^F(298.15 \text{ K})\} / (\text{kJ}\cdot\text{mol}^{-1}) = -5.44 \times 10^{-2} \{(\langle T \rangle / \text{K}) - 298.15\} \quad (3)$$

following the recommendation of Chickos et al.,<sup>11</sup> where  $\langle T \rangle$  is the temperature averaged over the temperature range covered by the experiments. Using eq 3, the observed value of  $\Delta_f^g H_m^F(\langle T \rangle)$ , the standard molar enthalpy of vaporization at  $T = 298.15$  K, was calculated (see Tables 6 and 7).

## 4. Discussion

### 4.1. Comparison of the Reaction Enthalpies Obtained from Equilibrium Studies and from Combustion

**Table 6. Thermochemical Results at  $T = 298.15$  K ( $p^\circ = 0.1$ MPa)**

	$\Delta_c u^\circ(\text{liq})$ J·g <sup>-1</sup>	$\Delta_c H_m^\circ(\text{liq})$ kJ·mol <sup>-1</sup>	$\Delta_f H_m^\circ(\text{liq})$ kJ·mol <sup>-1</sup>	$\Delta_f^\circ H_m^\circ$ kJ·mol <sup>-1</sup>	$\Delta_f H_m^\circ(\text{g})$ kJ·mol <sup>-1</sup>
methyl cumyl ether	-38 168.9 ± 2.7 <sup>a</sup>	-5742.5 ± 2.1 <sup>a</sup>	-193.4 ± 2.5 <sup>a</sup>	52.85 ± 0.16 <sup>a</sup>	-140.5 ± 2.5 <sup>a</sup>
ethyl cumyl ether	-38 821.5 ± 2.5	-6385.1 ± 2.3	-230.2 ± 2.7	54.70 ± 0.52	-175.5 ± 2.7
propyl cumyl ether <sup>b</sup>			-257.4 ± 2.4 <sup>c</sup>	59.31 ± 0.20	-198.1 ± 2.4
butyl cumyl ether	-39 939.3 ± 0.5	-7691.6 ± 2.6	-282.3 ± 3.1	63.84 ± 0.50	-218.5 ± 3.1

<sup>a</sup> Data from our previous work.<sup>3</sup> <sup>b</sup> Compound was not pure enough for the combustion experiments (see experimental part). <sup>c</sup> Calculated from the results of the chemical equilibrium study (see text).

**Table 7. Results from Measurements of the Vapor Pressure  $p$  of Alkyl Cumyl Ethers Using the Transpiration Method**

$T^a/\text{K}$	$m^b/\text{mg}$	$V(\text{N}_2)^c/\text{dm}^3$	$p^d/\text{Pa}$	$T^a/\text{K}$	$m^b/\text{mg}$	$V(\text{N}_2)^c/\text{dm}^3$	$p^d/\text{Pa}$
Ethyl Cumyl Ether $\ln(p/\text{Pa}) = (26.03 \pm 0.21) - (6594 \pm 62)(T/\text{K})^{-1}$							
278.3	1.85	2.77 <sup>e</sup>	10.43	298.4	1.53	0.446 <sup>e</sup>	52.31
283.3	2.11	2.07 <sup>e</sup>	15.72	303.2	2.99	0.646 <sup>f</sup>	70.59
288.2	2.27	1.56 <sup>f</sup>	22.68	303.3	1.56	0.311 <sup>e</sup>	76.06
288.4	2.18	1.42 <sup>e</sup>	23.52	308.1	3.50	0.534 <sup>f</sup>	99.71
293.2	2.80	1.30 <sup>f</sup>	33.30	308.4	1.60	0.225 <sup>e</sup>	107.5
293.5	2.22	0.959 <sup>e</sup>	35.23	313.2	1.69	0.180 <sup>e</sup>	142.4
298.2	2.78	0.869	48.99				
$\Delta_f^\circ H_m^\circ(T=295.7 \text{ K}) = (54.83 \pm 0.52) \text{ kJ}\cdot\text{mol}^{-1}$ ; $\Delta_f^\circ H_m^\circ(298.15 \text{ K}) = (54.70 \pm 0.52) \text{ kJ}\cdot\text{mol}^{-1}$							
Propyl Cumyl Ether $\ln(p/\text{Pa}) = (26.92 \pm 0.08) - (7110 \pm 24)(T/\text{K})^{-1}$							
278.3	8.11	30.05	3.847	310.2	5.82	1.48	54.75
293.2	5.54	5.33	14.55	313.2	6.30	1.28	68.52
298.2	5.37	3.43	21.83	316.2	6.19	1.02	84.39
301.3	5.79	2.88	28.05	319.2	6.00	0.804	103.8
304.3	6.97	2.82	34.46	322.2	6.01	0.660	126.7
307.3	5.37	1.72	43.45	325.2	6.22	0.559	154.7
$\Delta_f^\circ H_m^\circ(T=301.7 \text{ K}) = (59.12 \pm 0.20) \text{ kJ}\cdot\text{mol}^{-1}$ ; $\Delta_f^\circ H_m^\circ(298.15 \text{ K}) = (59.31 \pm 0.20) \text{ kJ}\cdot\text{mol}^{-1}$							
Butyl Cumyl Ether $\ln(p/\text{Pa}) = (27.85 \pm 0.21) - (7678 \pm 60)(T/\text{K})^{-1}$							
278.3	0.562	6.09 <sup>f</sup>	1.240	298.3	1.37	2.16 <sup>e</sup>	8.205
283.1	2.93	19.11 <sup>e</sup>	2.002	303.2	0.850	0.845 <sup>f</sup>	13.01
283.1	1.32	8.71 <sup>f</sup>	2.005	303.4	1.76	1.83 <sup>e</sup>	12.43
288.2	0.823	3.13 <sup>f</sup>	3.441	308.2	1.19	0.830 <sup>f</sup>	18.52
290.2	1.16	3.57 <sup>e</sup>	4.211	308.3	1.23	0.855 <sup>e</sup>	18.59
293.2	0.601	1.44 <sup>f</sup>	5.429	313.2	1.27	0.585 <sup>e</sup>	27.90
293.5	1.20	2.81 <sup>e</sup>	5.538	318.3	1.09	0.345 <sup>e</sup>	40.59
298.2	0.902	1.42 <sup>f</sup>	8.235				
$\Delta_f^\circ H_m^\circ(T=298.1 \text{ K}) = (63.84 \pm 0.50) \text{ kJ}\cdot\text{mol}^{-1}$ ; $\Delta_f^\circ H_m^\circ(298.15 \text{ K}) = (63.84 \pm 0.50) \text{ kJ}\cdot\text{mol}^{-1}$							

<sup>a</sup> Temperature of saturation, N<sub>2</sub> gas flow 0.22–0.42 cm<sup>3</sup>·s<sup>-1</sup>. <sup>b</sup> Mass of transferred sample condensed at  $T = 243$  K. <sup>c</sup> Volume of nitrogen used to transfer mass  $m$  of sample. <sup>d</sup> Vapor pressure at temperature  $T$ , calculated from  $m$  and the residual vapor pressure at 243 K. <sup>e</sup> N<sub>2</sub> gas flow 0.42 cm<sup>3</sup>·s<sup>-1</sup>. <sup>f</sup> N<sub>2</sub> gas flow 0.22 cm<sup>3</sup>·s<sup>-1</sup>.

**Table 8. Strain Enthalpies of Cumyl Derivatives at  $T = 298.15$  K**

	$\Delta_f H_m^\circ(\text{g})(\text{exp})$ kJ·mol <sup>-1</sup>	$\Delta_f H_m^\circ(\text{g})(\text{calc})^a$ kJ·mol <sup>-1</sup>	$H_S^b$ kJ·mol <sup>-1</sup>
cumyl alcohol ( $\alpha, \alpha$ -dimethylbenzyl alcohol)	-168.1 ± 2.4 <sup>c</sup>	-176.8	8.7
methyl cumyl ether	-140.5 ± 2.5 <sup>d</sup>	-151.4	10.9
ethyl cumyl ether	-175.5 ± 2.7	-184.5	9.0
propyl cumyl ether	-198.1 ± 2.4	-205.9	7.8
butyl cumyl ether	-218.5 ± 3.1	-227.4	8.9

<sup>a</sup> Calculated as the sum of strain-free increments (see text). <sup>b</sup> Strain enthalpy of cumyl derivatives  $H_S = \Delta_f H_m^\circ(\text{g})(\text{exp}) - \Delta_f H_m^\circ(\text{g})(\text{calc})$ . <sup>c</sup> The result was taken from Verevkin.<sup>19</sup> <sup>d</sup> The result was taken from Heintz and Verevkin.<sup>3</sup>

**tion Experiments.** We investigated the chemical equilibrium of reactions of the synthesis of alkyl cumyl ethers from  $n$ -alkanols and  $\alpha$ -methylstyrene in the temperature range (300 to 393) 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 enthalpies of formation  $\Delta_f H_m^\circ(\text{l})$  of ethyl and butyl cumyl ethers at 298.15 K were measured by means of combustion calorimetry in this work (Table 6). Further experimental data necessary for comparison are available in the literature: for  $\alpha$ -methylstyrene<sup>12</sup>  $\Delta_f H_m^\circ(\text{l}) = (70.07 \pm 0.82) \text{ kJ}\cdot\text{mol}^{-1}$  and for ethanol<sup>13</sup>  $\Delta_f H_m^\circ(\text{l}) = (-277.0 \pm 0.3)$

kJ·mol<sup>-1</sup>. Data for propanol,  $\Delta_f H_m^\circ(\text{l}) = (-302.5 \pm 0.2) \text{ kJ}\cdot\text{mol}^{-1}$ , and for butanol,  $\Delta_f H_m^\circ(\text{l}) = (-327.0 \pm 0.2) \text{ kJ}\cdot\text{mol}^{-1}$ , were taken from Mosselman and Dekker.<sup>14</sup> These data were used to calculate independently  $\Delta_f H_m^\circ(\text{calorimetry})$  of the alkyl cumyl ether synthesis reaction in the liquid phase (e.g. for ethyl cumyl ether):

$$\Delta_f H_m^\circ(\text{l})_{(\text{calorimetry})} = \Delta_f H_m^\circ(\text{l})_{(\text{EtCE})} - \Delta_f H_m^\circ(\text{l})_{(\text{EtOH})} - \Delta_f H_m^\circ(\text{l})_{(\alpha\text{-MS})} = -(24.0 \pm 2.6) \text{ kJ}\cdot\text{mol}^{-1}$$

The comparison with experimental values obtained from the chemical equilibrium study is given in Table 4. The calculated values of  $\Delta_f H_m^\circ(\text{l})_{(\text{calorimetry})}$  for the reactions of methyl, ethyl, and butyl cumyl ethers are in very close

agreement (within the boundaries of experimental uncertainties) with those  $\Delta_f H_m^{\circ}(l)_{(\text{equilibrium})}$  derived from the chemical equilibria studies. Hence, the important assumption that values of  $K_x$  in excess alkanol are indistinguishable from the thermodynamic constants  $K_a$  could be generalized for ether synthesis reactions.

The thermodynamic consistency observed allows us to calculate the enthalpy of formation of propyl cumyl ether  $\Delta_f H_m^{\circ}(l) = -(257.4 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$  from the known enthalpies of formation of propanol and  $\alpha$ -methylstyrene and the standard enthalpy of reaction obtained from the temperature dependence of  $K_x$  (see Table 6).

**4.2. Strain Enthalpies  $H_S$  of Alkyl Cumyl Ethers.** An important test to establish the validity of the experimental and calculation procedures presented in this paper provides the comparison of strain enthalpies of alkyl cumyl ethers, which could be derived from their gaseous standard molar enthalpies of formation  $\Delta_f H_m^{\circ}(g)$  at 298.15 K (Table 6). Indeed, the methyl, ethyl, propyl, and butyl cumyl ethers listed in Table 6 present a typical example of the homological. It is well established that for homologous rows such as alkanes or alkanols<sup>14</sup> the enthalpic contribution to  $\Delta_f H_m^{\circ}(g)$  from the  $\text{CH}_2$  group should remain constant. In other words, no additional strain interactions in a molecule are expected by passing from methyl to butyl cumyl ether. The resulting values of  $\Delta_f H_m^{\circ}(g)$  of alkyl cumyl ether calculated as the sum of  $\Delta_f H_m^{\circ}(l)$  and  $\Delta_f^{\circ} H_m^{\circ}$  are shown in Tables 6 and 8.

We define the strain enthalpy  $H_S$  of a molecule as the difference between the experimental standard enthalpy of formation  $\Delta_f H_m^{\circ}(g)$  and the calculated sum of the strain-free Benson type increments<sup>4</sup> for this molecule. The strain-free increments for the calculation of enthalpies of formation of alkanes,<sup>15</sup> alkylbenzenes,<sup>16</sup> and ethers<sup>17,18</sup> are already well established. By using these group-additivity parameters and the values of  $\Delta_f H_m^{\circ}(g)$  of cumyl derivatives (Table 8), their values of strain enthalpies  $H_S = \{\Delta_f H_m^{\circ}(g) - \Sigma \text{ increments}\}$  have been estimated (Table 8).

All alkyl cumyl ethers studied here are very similarly strained by about  $10 \text{ kJ}\cdot\text{mol}^{-1}$  (Table 8). This fact is a further indication that the data for  $\Delta_f H_m^{\circ}(g)$  of alkyl cumyl ethers, obtained by combining the different experimental techniques (calorimetry, transpiration, equilibrium study), are generally consistent, supporting the confidence in the experimental procedures used. To ascertain the strain effect, we also involved in the interpretation our recent result (see Table 8) for cumyl alcohol.<sup>19</sup> Cumyl alcohol also exhibits an amount of strain similar to that for alkyl cumyl ethers (see Table 8). What reasons cause strain in these molecules? Elucidation of the nature of strain in alkyl cumyl ethers is aided by comparison with the strain of the similar shaped *tert*-butylbenzene,<sup>20</sup>  $\Delta_f H_m^{\circ}(g) = -(24.42 \pm 0.80) \text{ kJ}\cdot\text{mol}^{-1}$ , and the strain enthalpy,  $H_S = 10.9 \text{ kJ}\cdot\text{mol}^{-1}$ . *tert*-Butylbenzene is a relevant structural pattern of strain in the cumyl derivatives 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 quaternary carbon atom. It is expected from the analogy with the strain of *tert*-butylbenzene that the observed amount of destabilization in cumyl derivatives could no doubt be attributed to the steric repulsions of methyl groups and the benzene ring attached to the central quaternary carbon atom. Because cumyl ethers and cumyl alcohol are strained similarly by about 8 to  $10 \text{ kJ}\cdot\text{mol}^{-1}$  (Table 8), it is evident that strain in cumyl derivatives is governed only by steric interactions of methyl groups and the benzene ring while the OH or alkoxy group is rather

devoid of steric interaction and apparently does not contribute to strain. Because of this, one can ensure that no additional group-additivity parameters or correction terms are necessary (besides the correction for strain  $H_S = 10.9 \text{ kJ}\cdot\text{mol}^{-1}$  like in *tert*-butylbenzene) for the group-contribution correlation for  $\Delta_f H_m^{\circ}(g)$  of alkyl cumyl ethers.

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