

# Reaction Equilibria in the Synthesis of 2-Methoxy-2-methylbutane and 2-Ethoxy-2-methylbutane in the Liquid Phase

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Equilibrium constants for the liquid-phase synthesis of 2-methoxy-2-methylbutane (TAME) and 2-ethoxy-2-methylbutane (TAEE) were measured in the temperature range 323–363 K. The equilibria were studied using the alcohol/alkene mixture in various mole ratios and the respective ether as a reagent in a batch reactor. A commercial cation exchange resin (Amberlyst 16) was used as the catalyst. The system was strongly nonideal, and the UNIQUAC estimation method was used in the calculation of the liquid-phase activity coefficients. The experimental equilibrium constants are given as a function of temperature. At 333 K the equilibrium constants  $K_a$  for the synthesis of TAME were  $39.6 \pm 2.5$  from methanol and 2-methyl-1-butene (2M1B) and  $4.1 \pm 0.3$  from 2-methyl-2-butene (2M2B). The equilibrium constants for the synthesis of TAEE were  $17.4 \pm 1.1$  from ethanol and 2M1B and  $1.7 \pm 0.1$  from 2M2B. The experimental  $\Delta_r H$  values for the liquid-phase synthesis of TAME were  $-33.6 \pm 5.1$  kJ·mol<sup>-1</sup> (2M1B) and  $-26.8 \pm 2.3$  kJ·mol<sup>-1</sup> (2M2B), and those for the synthesis of TAEE were  $-35.2 \pm 5.8$  kJ·mol<sup>-1</sup> (2M1B) and  $-27.3 \pm 6.7$  kJ·mol<sup>-1</sup> (2M2B). The results were compared with the literature values.

## Introduction

Tertiary ethers are used as octane-enhancing components in gasoline. Although 2-methoxy-2-methylpropane (methyl *tert*-butyl ether, MTBE) is currently being produced in large scale, the interest in the heavier tertiary ethers continues to increase steadily. At least 2-methoxy-2-methylbutane (*tert*-amyl methyl ether, TAME), 2-ethoxy-2-methylpropane (ethyl *tert*-butyl ether, ETBE), and 2-ethoxy-2-methylbutane (*tert*-amyl ethyl ether, TAEE) have been found to be suitable octane boosters (1, 2).

TAME and TAEE are synthesized in an acid-catalyzed, equilibrium reaction of isoamylenes (2-methyl-1-butene, 2M1B, or 2-methyl-2-butene, 2M2B) with methanol and ethanol, respectively. 3-Methyl-1-butene is not reactive in the etherification reaction under the same reaction conditions as 2M1B or 2M2B (3). The isoamylenes 2M1B and 2M2B form the third equilibrium in the system. The networks and our nomenclature for the reactions are presented in Figure 1.

Theoretical and experimental investigations from the equilibrium of the synthesis of MTBE have been published (4, 5). So far, there are only a few papers reporting experimental investigations of TAME (3, 6–9) and TAEE (2). In earlier studies we observed that under the conditions investigated the exothermal synthesis of these ethers was strongly thermodynamically limited even at temperatures below 343 K (2, 3). The reactivity of the isoamylenes was also clearly different with methanol than with ethanol (2). Safronov *et al.* studied the equilibrium of the synthesis of TAME, but they lumped the two isoamylenes (2M1B and 2M2B) together in their calculations and did not calculate the equilibrium constants for the two etherification reactions separately. The separate equilibrium constants of the etherification reactions are needed for our development of kinetic models of the etherification reactions to be pub-

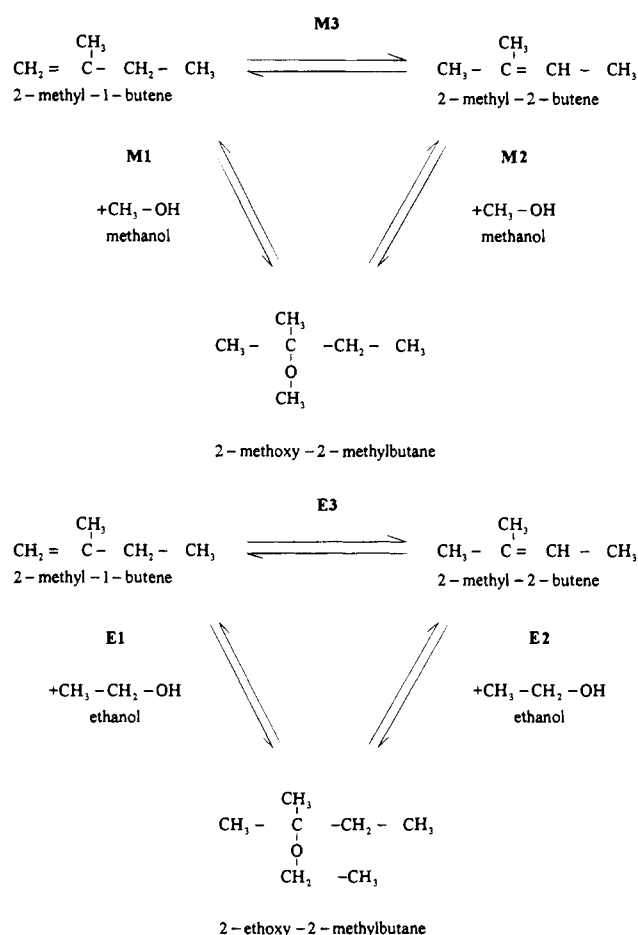


Figure 1. Reaction networks in the synthesis of TAME and TAEE: reactions M1, M2, M3, E1, E2, and E3.

lished later. In this paper we present the equilibrium constants for the liquid-phase synthesis of TAME and TAEE. These equilibrium constants are compared with the ones based on thermodynamic data.

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**Table 1. Thermodynamic Data (298 K, 1 atm, Liquid Phase) from the Thermodynamics Research Center (13), CRC Handbook of Chemistry and Physics (14), and AIChE Data Compilation (15)**

quantity	unit	MeOH		EtOH		2M1B		2M2B		TAME		TAE	
$\Delta H^{\circ}$ (liq)	$\text{kJ}\cdot\text{mol}^{-1}$	-238.46	(14)	-277.50	(14)	-60.96	(13)	-68.07	(13)	-334.9	(13)	-372.9	(13)
$\Delta G^{\circ}$ (liq)	$\text{kJ}\cdot\text{mol}^{-1}$	-166.15	(14)	-174.68	(14)	66.5	(13)	60.0	(13)	-108.2	(13)	-119.9	(13)
$S^{\circ}$ (liq)	$\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	0.1267	(14)	0.1606	(14)	0.254	(13)	0.2521	(13)	0.2905	(13)	0.339	(13)
$c_p$ (liq)	$\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	0.0816	(14)	0.1130	(14)	0.1569	(14)	0.1523	(14)	0.2192	(13)	0.244	(13)
$c_p^a$	$a \times 10^2$	10.76	(15)	9.456	(15)	14.951	(15)	15.4	(15)	7.83	(15)	b	
	$b \times 10^6$	-38.06	(15)	-5.62	(15)	-24.763	(15)	-29.335	(15)	44.92	(15)		
	$c \times 10^7$	9.79	(15)	-3.29	(15)	9.1849	(15)	9.794	(15)				
	$d \times 10^9$			2.398	(15)								

<sup>a</sup> The equation of temperature dependence for  $c_p = a + bT + cT^2 + dT^3$ . <sup>b</sup> Temperature dependence of  $c_p$  for TAE estimated to be the same as for TAME.

**Table 2. Experimental Reaction Conditions (Temperature and Initial Alcohol/Isoamylene Mole Ratio), Measured Mole Fractions, and Equilibrium Constants for the Synthesis of TAME**

T/K	init mole ratio	$x_{\text{MeOH}}$	$x_{\text{2M1B}}$	$x_{\text{2M2B}}$	$x_{\text{TAME}}$	$K_x(\text{exptl})$			$K_a(\text{exptl})$		
						M1	M2	M3	M1	M2	M3
323	TAME <sup>a</sup>	0.195	0.015	0.166	0.604	206.5	18.7	11.1	64.2	5.7	11.2
323	1.0	0.202	0.014	0.131	0.618	218.5	23.4	9.4	64.9	5.8	11.1
333	TAME <sup>a</sup>	0.219	0.019	0.194	0.557	133.2	13.1	10.2	41.3	4.0	10.4
333	0.1	0.003	0.070	0.735	0.132	721.2	69.1	10.4	85.6	8.6	9.9
333	0.5	0.047	0.041	0.416	0.481	250.2	24.6	10.2	44.4	4.4	10.1
333	1.0	0.221	0.021	0.188	0.560	121.2	13.5	9.0	37.9	4.2	9.1
333	2.5	0.636	0.005	0.054	0.298	88.4	8.7	10.2	48.7	4.5	10.7
333	5.0	0.794	0.003	0.026	0.174	84.3	8.5	9.9	48.0	4.5	10.4
333	10.0	0.900	0.001	0.011	0.085	94.1	8.4	11.2	48.0	4.3	11.8
343	TAME <sup>a</sup>	0.257	0.028	0.212	0.490	69.1	9.0	7.7	31.3	3.4	9.3
343	1.0	0.271	0.021	0.204	0.491	84.7	8.9	9.5	29.8	3.1	9.8
353	TAME <sup>a</sup>	0.266	0.029	0.247	0.448	58.2	6.8	8.5	20.9	2.4	8.7
353	0.1 <sup>b</sup>	0.006	0.077	0.694	0.137	306.8	34.0	9.0	41.8	4.9	8.6
353	0.13 <sup>b</sup>	0.011	0.071	0.634	0.172	219.6	24.7	8.9	37.2	4.4	8.6
353	0.5	0.080	0.051	0.447	0.403	98.6	11.3	8.7	20.8	2.4	8.7
353	1.0	0.270	0.028	0.243	0.446	60.1	6.8	8.8	21.0	2.3	9.0
353	2.5	0.633	0.009	0.081	0.268	45.0	5.2	8.6	24.8	2.7	9.1
353	5.0	0.804	0.005	0.038	0.147	40.6	4.8	8.4	23.0	2.6	8.9
353	10.0	0.900	0.002	0.016	0.078	45.6	5.4	8.4	24.2	2.7	9.2
363	TAME <sup>a</sup>	0.290	0.032	0.257	0.399	43.4	5.4	8.1	15.9	1.92	8.3

<sup>a</sup> Initial feed TAME. <sup>b</sup> Significant formation of dimers.

## Experimental Section

**Catalyst and Chemicals.** A commercial macroreticular strong cation exchange resin in H<sup>+</sup> form (Amberlyst 16, Rohm & Haas) was used as the catalyst. The cross-linking level of the resin was 12 mass % and the exchange capacity 5.2 mmol/g<sub>dry catalyst</sub> measured with the method described by Fisher and Kunin (10). The catalyst was treated with the respective alcohol at room temperature prior to the experiments in order to remove the water from the catalyst pores.

The following reagents were used in the experiments: The 2-methyl-2-butene was technical grade (Fluka Chemika) with a composition of 2-methyl-2-butene (90.7 mass %), 2-methyl-1-butene (8.6 mass %), and impurities (0.7 mass %). The alcohols were MeOH (>99.8 mass %, Merck) and EtOH (>99.5 mass %, Alko). TAE (>97.0 mass %) and TAME (>97.2 mass %) required for the splitting reactions were distilled from reaction products produced by Yarsintez, Russia.

**Apparatus.** The experiments to determine the reaction equilibrium compositions were carried out in a batch reactor (80 cm<sup>3</sup>, stainless steel vessel). The reaction mixture was stirred magnetically, and the temperature was controlled within  $\pm 0.25$  K by immersing the reactor in a thermostated water bath. To guarantee a liquid-phase operation at every temperature, the pressure was set at 0.7 MPa. The catalyst (1 g) was placed in a metal gauze basket (60 mesh), which simultaneously worked as a mixing baffle in the reactor. The samples from the reaction mixture were taken manually via a sample valve at the top of the reactor. The samples were taken successively

until no further change was observed in the product composition.

**Analysis.** The products were analyzed with a Hewlett-Packard gas chromatograph 5990 Series II equipped with a flame ionization detector using a HP 3396A integrator. The compounds were separated in a glass capillary column DB-1 (length 60 m, film thickness 1.0  $\mu\text{m}$ , column diameter 0.254 mm; J & W Scientific). During the experiments the response factors of the reagents and solvents were regularly checked with calibration solutions. In the calculations the experimental error for the gas chromatographic analysis was assumed to be 1 mass % for each component. The mass balance of the reagents and products was checked in the experiments by comparing the moles of reacted reagents to the moles of formed products.

**Feed.** In addition to the mixture of alcohol/isoamylene in various mole fractions, the two ethers were used as a reagent to confirm the equilibrium state at different temperatures.

The effects of the initial mole ratio of alcohol/isoamylene and temperature on the equilibria of etherification reactions were measured. The alcohol/isoamylene mole ratio was varied between 0.1 and 10 and the temperature between 323 and 363 K in the TAME experiments and between 323 and 353 K in the TAE experiments.

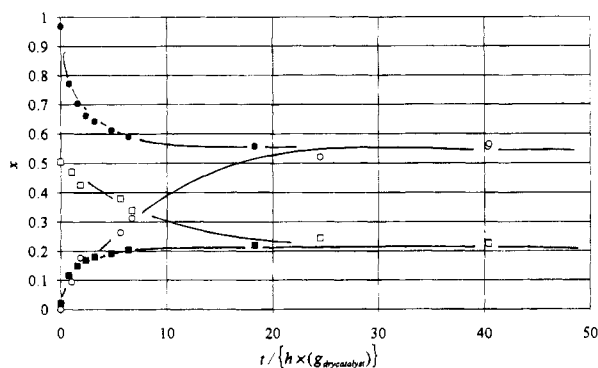
## Calculation and Equations

The mole fractions of the products and the reagents under equilibrium conditions were used in the calculation of the mole fraction equilibrium ratio  $K_x$ :

**Table 3. Experimental Reaction Conditions (Temperature and Initial Alcohol/Isoamylene Mole Ratio), Measured Mole Fractions, and Equilibrium Constants for the Synthesis of TAE**

T/K	init mole ratio	$x_{\text{ETOH}}$	$x_{2\text{M1B}}$	$x_{2\text{M2B}}$	$x_{\text{TAE}}$	$K_x(\text{exptl})$			$K_a(\text{exptl})$		
						E1	E2	E3	E1	E2	E3
323	TAE <sup>a</sup>	0.278	0.022	0.293	0.444	73.9	6.7	11.1	25.4	2.3	11.0
323	1.0	0.285	0.022	0.243	0.430	68.9	6.2	11.1	24.1	2.1	11.0
333	TAE <sup>a</sup>	0.315	0.026	0.264	0.374	45.8	4.5	10.2	17.1	1.6	10.2
333	0.1	0.008	0.075	0.773	0.118	207.3	20.1	10.3	25.2	2.6	10.3
333	0.13	0.009	0.072	0.750	0.146	222.8	21.4	10.4	27.6	2.8	10.4
333	1.0	0.312	0.026	0.263	0.385	48.2	4.7	10.3	17.7	1.7	10.2
333	7.5	0.873	0.004	0.037	0.084	26.0	2.6	9.9	13.9	1.4	10.6
333	10.0	0.904	0.003	0.026	0.064	26.0	2.7	9.8	13.9	1.3	10.9
343	TAE <sup>a</sup>	0.345	0.031	0.291	0.307	28.6	3.1	9.4	11.3	1.2	9.3
343	1.0	0.346	0.031	0.293	0.310	28.5	3.1	9.3	11.3	1.2	9.3
353	TAE <sup>a</sup>	0.373	0.034	0.308	0.255	19.3	2.2	8.7	8.0	0.9	8.7
353	0.1 <sup>b</sup>	0.017	0.084	0.748	0.105	73.6	8.3	8.9	10.3	1.2	8.8
353	0.13 <sup>b</sup>	0.018	0.085	0.752	0.110	70.8	8.0	8.9	10.3	1.2	8.8
353	1.0	0.385	0.035	0.291	0.268	20.2	2.4	8.4	8.5	1.0	8.4
353	7.5	0.877	0.006	0.048	0.066	13.4	1.6	8.6	7.4	0.8	9.4
353	10.0	0.905	0.004	0.036	0.051	13.5	1.6	8.7	7.3	0.8	9.6

<sup>a</sup> Initial feed TAE. <sup>b</sup> Significant formation of dimers.



**Figure 2.** TAME and MeOH mole fractions  $x$  as a function of contact time at 333 K: TAME mole fraction in forward (○) and in splitting (●) experiments; MeOH mole fraction in forward (□) and in splitting (■) experiments.

$$K_x = \prod (x_i)^{\nu_i} \quad (1)$$

where  $x_i$  is the mole fraction and  $\nu_i$  the stoichiometric coefficient of component  $i$ .  $K_x$  was calculated both for the etherification reactions (see Figure 1, reactions M1, M2, E1, and E2) and for the isomerization reactions of the isoamylenes (Figure 1, reactions M3 and E3). Since similar etherification systems deviate clearly from ideality (5, 8, 11), it could be assumed that the equilibrium ratios,  $K_x$ , strongly depend on the composition of the equilibrium mixture. The nonideality was discussed earlier also by Krause and Hammarström (3) in the case of TAME synthesis. To compare the experimental equilibrium values  $K_a$  with the calculated ones  $K$ , which were determined from thermodynamic data, we need to present the experimental equilibrium in terms of activities,  $a_i$ :

$$K_a = \prod (a_i)^{\nu_i} = \prod (\gamma_i)^{\nu_i} \prod (x_i)^{\nu_i} \quad (2)$$

The activity coefficients,  $\gamma_i$ , have been calculated by the UNIQUAC method.

The equilibrium constant  $K$  could also be evaluated from the Gibbs free energy change for the reaction  $\Delta_r G$  at temperature  $T$  with

$$K = \exp(-\Delta_r G/RT) = \exp(-\Delta_r H/RT + \Delta_r S/R) \quad (3)$$

where  $\Delta_r H$  is the standard enthalpy change of reaction,  $\Delta_r S$  is the entropy change of the reaction, and  $R$  is the universal gas constant,  $8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

The temperature dependence of  $K$  is usually given by the van't Hoff equation:

$$\left[ \frac{\partial \ln K}{\partial T} \right] = \frac{\Delta_r H(T)}{RT^2} \quad (4)$$

The dependence of  $\Delta_r H$  on temperature could be computed by integration of the Kirchoff equation:

$$d\Delta_r H/dT = \sum \nu_i c_{pi} \quad (5)$$

where the heat capacity of component  $i$  could be expressed as  $c_{pi} = a_i + b_i T + c_i T^2 + d_i T^3$ .

The enthalpy change in the synthesis of the ether was assumed to be independent of temperature in the range investigated. Thus, eq 4 was written to a more simple form:

$$\ln K = -\Delta_r H/RT + c_1 \quad (6)$$

where the entropy change of reaction can be calculated from the integration constant with

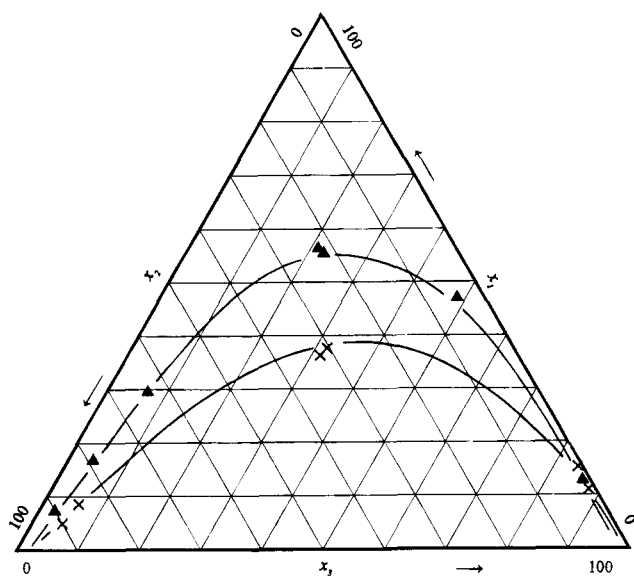
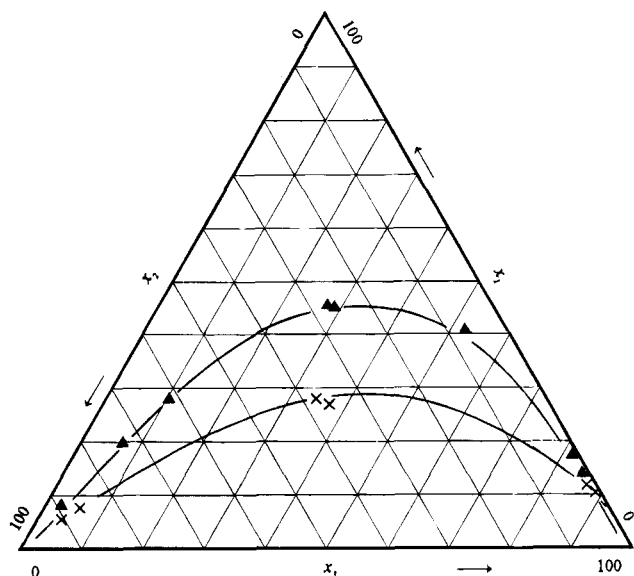
$$c_1 = \Delta_r S/R \quad (7)$$

The thermodynamic data for the components in the liquid phase used in the calculations are presented in Table 1.

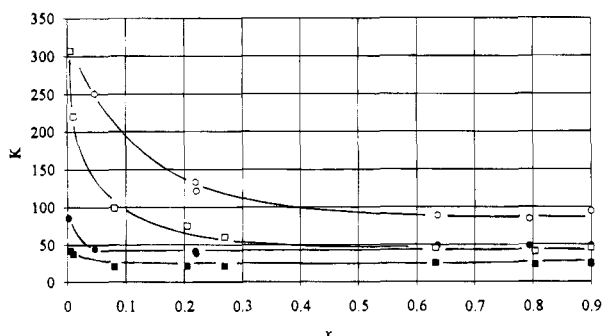
## Results and Discussion

In Figure 2 the TAME and MeOH mole fractions as a function of contact time are presented for two separate experiments where, respectively, an isoamylene/methanol mixture (mole ratio 1:1) and TAME were used as the initial reagent at 333 K. As seen in Figure 2 the mole fractions of TAME and MeOH became equal in the forward and splitting (i.e., the reverse reaction of ether to isoamylenes and alcohol) experiments after a contact time of about 20 h  $g_{\text{dry catalyst}}$ .

The reaction equilibria for the synthesis of TAME and TAE were measured by varying the initial mole ratio of alcohol/isoamylene between 0.1 and 10. Tables 2 and 3 show the results of each experiment: the experimental conditions, the mole fractions of the components in equilibrium, and  $K_x$  and  $K_a$  for the TAME and TAE reactions. The conditions of the equilibria are also presented graphically in three-component diagrams, Figure 3. Dimer formation was observed in the experiments with small alcohol/isoamylene ratios. The mole fraction equilibrium ratios,  $K_x$ , depended strongly on the composition of the



**Figure 3.** Ether (1), alcohol (2), and isoamylenes (3) mole fractions in equilibrium: (a, top) MeOH-TAME-isoamylenes (▲) and EtOH-TAEE-isoamylenes (×) mole fractions in equilibrium at 353 K; (b, bottom) MeOH-TAME-isoamylenes (▲) and EtOH-TAEE-isoamylenes (×) mole fractions in equilibrium at 333 K.



**Figure 4.**  $K_x$  and  $K_a$  for TAME synthesis as a function of methanol mole fraction  $x$  in the equilibrium state:  $K_x$  (○) and  $K_a$  (●) at 333 K;  $K_x$  (□) and  $K_a$  (■) at 353 K.

equilibrium mixture. In our experiments the mixture was strongly nonideal, especially when the mole fraction of alcohol was low and the activity coefficient of the alcohol then differed considerably from that of the other compounds in the mixture. By way of illustration, Figure 4 shows  $K_x$  and  $K_a$  as a function of the alcohol mole fraction

**Table 4.** Equilibrium Constants for the Synthesis of TAME and TAEE at Different Temperatures: Experimental  $K_a$  and  $K$  Calculated from the Thermodynamic Data

Formation of TAME						
T/K	$K_a$ (exptl)			$K$ (thermodyn)		
	M1	M2	M3	M1	M2	M3
323	64.5 ± 4.8	5.8 ± 0.4	11.2 ± 0.4	10.5	0.94	11.0
333	39.6 ± 2.5	4.1 ± 0.3	9.7 ± 0.4	7.0	0.68	10.1
343	30.5 ± 1.9	3.2 ± 0.2	9.6 ± 0.4	4.8	0.50	9.3
353	20.9 ± 1.3	2.40 ± 0.15	8.9 ± 0.4	3.3	0.37	8.7
363	15.9 ± 1.2	1.92 ± 0.14	8.3 ± 0.3	2.3	0.27	8.1

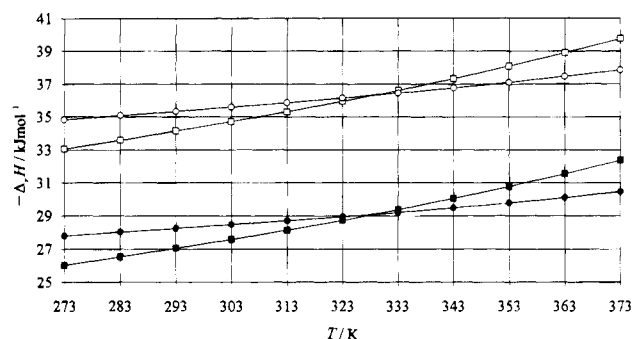
Formation of TAEE						
T/K	$K_a$ (exptl)			$K$ (thermodyn)		
	E1	E2	E3	E1	E2	E3
323	24.8 ± 1.5	2.2 ± 0.1	10.99 ± 0.4	32.6	3.6	11.0
333	17.4 ± 1.1	1.7 ± 0.1	10.19 ± 0.4	21.6	2.6	10.1
343	11.3 ± 0.8	1.19 ± 0.08	9.32 ± 0.4	14.7	1.9	9.3
353	8.3 ± 0.6	0.95 ± 0.07	8.55 ± 0.4	10.1	1.4	8.7
363				7.1	1.1	8.1

in equilibrium for the synthesis of TAME from methanol and 2M1B at temperatures of 333 and 353 K. The deviation of the system from ideality is clearly evident.

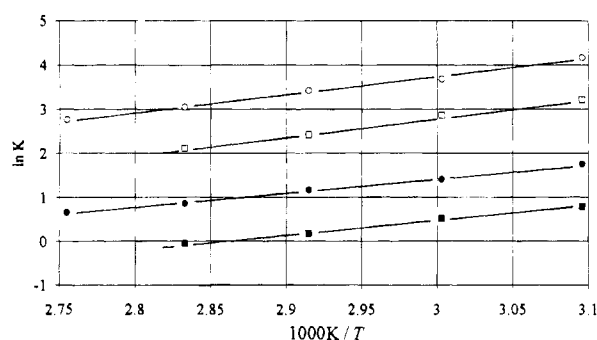
The experimental equilibrium constant,  $K_a$ , also deviated slightly from a constant value at the very low alcohol/isoamylenes initial ratio. In these experiments the mole fraction of alcohol was very low at equilibrium ( $<0.02$ ), as can be seen in Tables 2 and 3. A similar deviation was observed by Safronov *et al.* (8). The deviation at very low mole fractions may partly be due to the inaccuracies in the analysis, which is more difficult at small alcohol concentrations. The other source of the inaccuracy might be in the calculation of activity coefficients. Colombo *et al.* (5) note also in their paper that the predicted dependence of  $\gamma_{\text{MeOH}}$  values on concentration looks to be too low compared with the experimental results at  $x_{\text{MeOH}} < 0.01$ .

The experimental constants,  $K_a$ , which are presented numerically at different temperatures in Table 4, were calculated from the results in Tables 2 and 3, where either pure ether or alcohol/isoamylenes at a mole ratio of 1:1 was used as the reagent. For comparison the equilibrium constants  $K$  calculated from thermodynamic data in Table 1 are included in Table 4. For the isomerization reaction the calculated and experimental equilibrium constants are in very good agreement, but for the etherification reactions the differences are significant. For the synthesis of TAME, equilibrium conversions and equilibrium constants were considerably higher than the corresponding values calculated from the thermodynamic data. For the synthesis of TAEE the experimentally obtained and the calculated equilibrium constants were in much better agreement. The equilibrium constant  $K$  is highly sensitive to the thermodynamic data used in the calculations, as we discovered during our calculations. The influence of the enthalpy of formation  $\Delta_f H$  of a component on the equilibrium constant is the most significant; e.g. an increase of 1% in the value of  $\Delta_f H$  of TAME changed the value of  $K$  from 10.5 to 36.3 at 323 K. A similar difference in the absolute entropy of a component,  $S$  or  $c_p$ , had only a minor effect on  $K$ .

The temperature dependence of  $\Delta_f H$  was calculated using eq 5 and the thermodynamic data in Table 1. Figure 5 shows the  $\Delta_f H$  values for the synthesis of TAME and TAEE as a function of temperature. The temperature dependence of the liquid-phase heat capacity of TAEE could not be found in the literature, so we assumed it to be the same as that of TAME. The calculated dependence of  $\Delta_f H$  on temperature for the etherification reactions was evident in Figure 5. By contrast, in the temperature range 323–



**Figure 5.** Reaction enthalpy ( $-\Delta_r H$ ) of liquid-phase synthesis of TAME and TAEE as a function of temperature: synthesis of TAME from methanol and 2M1B (○) and from methanol and 2M2B (●); synthesis of TAEE from ethanol and 2M1B (□) or from ethanol and 2M2B (■).



**Figure 6.**  $\ln K_a$  as a function of reciprocal reaction temperature  $1/T$  for the synthesis of TAME from methanol and 2M1B (○) and from methanol and 2M2B (●);  $\ln K_a$  for the synthesis of TAEE from ethanol and 2M1B (□) and from ethanol and 2M2B (■).

**Table 5. Experimental Evaluated Enthalpy Change,  $\Delta_r H$ , and Entropy Change,  $\Delta_r S$ , of Reaction and 95% Confidence Intervals for the Values**

reaction	$\Delta_r H/$ (kJ·mol <sup>-1</sup> )	95% confidence interval	$\Delta_r S/$ (J·K <sup>-1</sup> mol <sup>-1</sup> )	95% confidence interval
M1	-33.6	±5.1	-69.7	±14.3
M2	-26.8	±2.3	-68.6	±6.6
M3	-6.7	±3.0	-0.86	±8.9
E1	-35.2	±5.8	-82.3	±17.3
E2	-27.3	±6.7	-77.8	±19.8
E3	-8.0	±1.4	-4.7	±4.2

363 K that was investigated experimentally we observed a linear dependence of  $\ln K_a$  on the reciprocal temperature (Figure 6) and could not see any difference in  $\Delta_r H$  at various temperatures. We therefore took  $\Delta_r H$  to be constant over the studied range, and calculated the  $\Delta_r H$  values for the synthesis of both ethers with the simplified equation (6). The experimental  $\Delta_r H$  and  $\Delta_r S$  values and their 95% confidence limits for liquid-phase synthesis of TAME and TAEE are presented in Table 5. The entropy change,  $\Delta_r S$ , of the isomerization reaction (M3 or E3) is not satisfactorily determined in our experiments; the 95% confidence intervals are very broad. The experimental  $\Delta_r H$  values are in agreement with the values which have been calculated from thermodynamic data: at 323 K, for example, the calculated  $\Delta_r H$  values for TAME and TAEE are  $-35.9$  (2M1B),  $-28.7$  (2M2B),  $-36.2$  (2M1B), and  $-29.0$  kJ·mol<sup>-1</sup> (2M2B). Our experimental results agreed with those reported in the literature; for the synthesis of TAME, Safronov *et al.* reported a value of  $-35.95$  kJ·mol<sup>-1</sup> (358 K) for  $\Delta_r H$  (8) and Randriamahefa and Gallo a value of  $-41.17$  kJ·mol<sup>-1</sup> (7) for both isoamylenes together in the liquid phase. From the results of Muja *et al.* (6) we also computed the  $\Delta_r H$  value for each isoamylenes separately, but the results differed significantly from ours. Frenkel

*et al.* (12) have published the enthalpy change and the entropy change of the isomerization of 2-methyl-1-butene to 2-methyl-2-butene in the gas phase at 562 K following  $\Delta_r H = -8.07 \pm 0.48$  kJ·mol<sup>-1</sup> and  $\Delta_r S = -5.02 \pm 0.84$  J·K<sup>-1</sup>·mol<sup>-1</sup>. Our results in the liquid phase are comparable to these values within the experimental uncertainties, while the heat of vaporization of the isomers are very close to each other and the temperature dependence of  $\Delta_r H$  of the isomerization reaction could be assumed to be small.

## Conclusions

The effects of the initial mole ratio of alcohol/isoamylenes and the reaction temperature on the reaction equilibria in the liquid-phase synthesis of TAME and TAEE were studied in a batch reactor. The equilibrium state was confirmed by using first the isoamylenes/alcohol mixture and then the respective ether as the reagent. The reaction mixtures were strongly nonideal, as the mole fraction equilibrium ratios,  $K_x$ , were observed to depend strongly on the alcohol mole fraction at equilibrium. The equilibrium conversion for the synthesis of TAME was considerably higher than for TAEE in the temperature range investigated. At 333 K the experimental equilibrium constants  $K_a$  for the synthesis of TAME were  $39.6 \pm 2.5$  (2M1B) and  $4.1 \pm 0.3$  (2M2B) and for TAEE  $17.4 \pm 1.1$  (2M1B) and  $1.7 \pm 0.1$  (2M2B) at 333 K. The enthalpy change of the reaction,  $\Delta_r H$ , for the liquid-phase synthesis of TAME from methanol was determined to be  $-33.6 \pm 5.1$  kJ·mol<sup>-1</sup> with 2M1B and  $-26.8 \pm 2.3$  kJ·mol<sup>-1</sup> with 2M2B and, correspondingly, for the synthesis of TAEE from ethanol  $-35.2 \pm 5.8$  kJ·mol<sup>-1</sup> with 2M1B and  $-27.3 \pm 6.7$  kJ·mol<sup>-1</sup> with 2M2B. The experimental  $\Delta_r H$  values for the etherification reactions agreed well with the values calculated from thermodynamic data.

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