

# Dehydration of the Alcohol in the Etherification of Isoamylenes with Methanol and Ethanol

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The kinetics of the dehydration of methanol and ethanol, which is a side reaction in the synthesis of tertiary ethers (TAME, 2-methoxy-2-methylbutane; TAEE, 2-ethoxy-2-methylbutane), were investigated in a continuous stirred tank reactor, with a commercial ion-exchange resin (Amberlyst 16) used as the catalyst. The effect of the alcohol concentration on the formation rates of dimethyl ether (DME) and diethyl ether (DEE) was measured between 323 and 363 K. The formation of the dialkyl ethers was favored by high temperatures and high-alcohol concentrations. At higher temperatures DME formed at a faster rate than DEE. The experimental results were best described with a model where one alcohol molecule is adsorbed and the other reacts from the liquid phase. Kinetic models for the synthesis of TAME and TAEE, expanded with the dehydration reactions and written in terms of component activities, are presented. The UNIFAC method was applied for the calculation of activity coefficients. The activation energy was determined to be 102.6 kJ/mol for methanol dehydration to yield DME and 90.5 kJ/mol for ethanol dehydration to yield DEE.

## Introduction

The new reformulated gasoline requirements already legislated in the United States, and many of the changes currently being considered in Europe for gasoline and diesel fuel present particularly challenging problems for refiners. The production of tertiary ethers will play a major role in meeting the new gasoline specifications, such as lower aromatics, olefins, and RVP (Simpson and Hibbs, 1995). The processing of FCC light gasoline with alcohol is one of the most economical methods for producing oxygenates to compensate for the octane deficits. In 1995, production capacities for the methanol-based tertiary ethers MTBE (methyl *tert*-butyl ether, 2-methoxy-2-methylpropane) and TAME (*tert*-amyl methyl ether, 2-methoxy-2-methylbutane) were 27.5 Mm<sup>3</sup>/a (473 250 b/d) and 2.5 Mm<sup>3</sup>/a (42 700 b/d), respectively (IRI, 1995). A major reason for growing interest in the ethanol-based tertiary ethers ETBE (ethyl *tert*-butyl ether, 2-ethoxy-2-methylpropane) and TAEE (*tert*-amyl ethyl ether, 2-ethoxy-2-methylbutane) is that ethanol can be produced by fermentation from renewable resources.

TAME and TAEE are synthesized in acid-catalyzed, equilibrium reactions of isoamylenes (2-methyl-1-butene, 2M1B, and 2-methyl-2-butene, 2M2B) with methanol and ethanol, respectively. The isomerization reaction between the two isoamylenes 2M1B and 2M2B establishes a third equilibrium. Typical side reactions are the dehydration of alcohol to yield dialkyl ether and water, hydration of isoamylenes to yield tertiary alcohol, and dimerization of isoamylenes.

So far, the majority of kinetic models published deal only with the main reactions. However, it is also important to investigate the formation of byproducts in the synthesis of the fuel oxygenates because of the

specifications that are defined within an oil refinery both for the gasoline product and for the intermediates. The etherification reactions are exothermic, and possible hot spots resulting from uneven cooling may lead to unwanted side reactions. The dehydration of the alcohol, both methanol (MeOH) and ethanol (EtOH), is a relevant side reaction because in the novel processes for producing tertiary ethers the alcohol/olefin ratio may be greater than the stoichiometric value, as the conversions to tertiary ethers are maximized by side reactor configuration or by catalytic distillation (Ignatius *et al.*, 1995; Patton *et al.*, 1995). Moreover, in a typical refinery the feed to the alkylation unit should be free of any oxygenates. Vila *et al.* (1994) studied the effect of temperature and the initial molar methanol/isobutene ratio on byproduct formation in MTBE synthesis in a batch reactor. The dimethyl ether formation was favored by high temperatures and high MeOH/IB molar ratios. The amount of DME formed at 355 K was correlated with the initial methanol concentration and the initial MeOH/IB molar ratio. Pavlova *et al.* (1986) have presented for TAME synthesis a complete activity-based kinetic model, which also includes the rate expression for DME formation.

Kinetic models have been published by our group for the synthesis of both TAME (Rihko *et al.*, 1997) and TAEE (Linnekoski *et al.*, 1997). The modeling took into account the nonideality of the liquid phase by expressing both the reaction equilibria and the kinetic equations as functions of component activities. In this study, we present expanded kinetic models for the synthesis of TAME and TAEE, where the dehydration of MeOH and EtOH are properly formulated as relevant side reactions.

## Experimental Section

The effects of temperature and reagent concentration on the formation rates of TAME and DME as well as TAEE and DEE were measured with various residence times.

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**Apparatus.** Reaction rates were measured in a continuous stirred tank reactor (CSTR, 55.6 cm<sup>3</sup>, stainless steel), where the reaction mixture was magnetically stirred. The stirrer speed was set to 950 rpm to eliminate the influence of external diffusion control on the reaction rates (Rihko and Krause, 1995). The catalyst (0.2–2.3 g) was placed in a metal gauze basket (60 mesh). The temperature (323–363 K) was controlled within  $\pm 0.2$  K by immersing the reactor in a thermostated water bath. The pressure was kept constant at 0.7–1.2 MPa to ensure a liquid phase operation at all temperatures. The pulse-free flow rate (5–82 g/h) of the feed was controlled by a liquid mass flow controller. A Mettler PM 6000 balance was used to measure the actual flow at the outlet of the reactor system. The composition of the feed and the reactor effluent were analyzed on-line with a gas chromatograph using an automated liquid sampling valve.

**Analysis.** Products were analyzed with a Hewlett-Packard gas chromatograph 5890 Series II, equipped with a flame ionization detector using a HP 3396A integrator. The compounds were separated in a glass capillary column HP-1 (length 60 m, thickness 1.0  $\mu$ m, column diameter 0.254 mm; Hewlett-Packard). Response factors were determined with calibration solutions.

**Chemicals and Catalyst.** The following reagents were used in the experiments: a mixture of isoamylenes (2M2B, 92 wt %, Fluka Chemika), methanol (>99.8 wt %, Riedel-de Haën), and ethanol (>99.5 wt %, Alko Oy). In some experiments, the reagents were diluted with isopentane (>99.0 wt %, Fluka Chemika). The ethers used for the GC calibration solutions were TAME (>98.5 wt %, Neste), TAE (E) (>97 wt %, Yarsintez), DME (>99.2 wt %, Fluka Chemika), and DEE (>95 wt %, Yarsintez). A commercial macroreticular strong cation ion-exchange resin in hydrogen form (Amberlyst 16, Rohm & Haas) was used as the catalyst. The cross-linking level of the resin was 12 wt %, and the exchange capacity 5.0 mmol/g of dry catalyst measured by the method described in standard ASTM D 2187 (1991). Unsieved catalyst particles that varied in size from 0.3 to 1.0 mm, the main fraction (71.3 wt %) being 0.5–0.8 mm, were used in the experiments according to our earlier studies where the influence of pore diffusion control has been checked (Rihko and Krause, 1995). Before the experiments, the catalyst was treated with the respective alcohol at room temperature to remove the water from the catalyst pores.

**Dehydration Experiments.** *Set I.* The basic DME and DEE experiments were carried out both with undiluted methanol and ethanol and with methanol and ethanol diluted with isopentane so that the molar fraction of the alcohol was 0.2 in the mixture. The residence time (i.e., amount of catalyst/mass flow rate) was varied from 0.06 to 0.31 h and the temperature range was 323–363 K.

*Set II.* To study the alcohol dehydration as a side reaction in the formation of tertiary ethers, we carried out runs where the amount of isoamylenes was kept constant (molar fraction of 0.1) while the alcohol/isoamylenes molar ratio was increased from 5 to 20. Isopentane was used as a solvent. The temperature range was 333–353 K and the residence time was varied from 0.06 to 0.31 h.

*Set III.* The effect of alcohol concentration on the reaction selectivity within a kinetic regime was studied for TAME. Runs were carried out at 353 K, where

shorter residence times 0.004–0.014 h were applied. In these experiments the methanol/isoamylenes molar ratio was varied between 1 and 9. Solvent was added in different amounts to obtain molar fractions of methanol between 0.2 and 0.8.

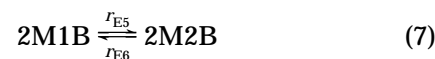
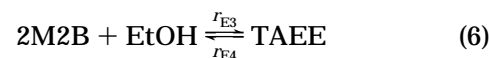
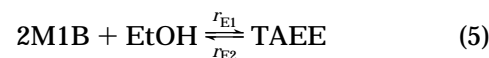
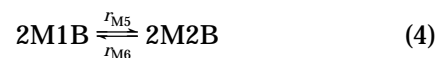
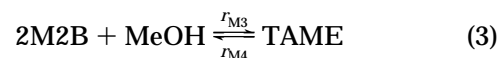
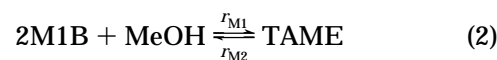
During the experiments the effects of the molar ratio of the reagents and the concentration of alcohol were studied in a random sequence, and in each set of different mixtures the temperature was varied randomly. The catalyst was changed after each set of mixtures. The stability of the catalyst was checked in each set of mixtures by repeating the experiment at first temperature after the experiments at the other temperatures had been carried out. The catalyst showed no deactivation even with the longest experiment (120 h). Depending on the residence time, it took about 4–5 h (set III) or 12–14 h (sets I and II) to attain a steady state in a CSTR.

The reaction rates  $r_i$  (mol kg<sub>cat</sub><sup>-1</sup> s<sup>-1</sup>) of the products TAME, DME, TAE (E), DEE, and TAA were calculated according to eq 1:

$$r_i = \frac{(F_{i,\text{out}} - F_{i,\text{in}})}{W_{\text{cat}}} = \frac{(w_{i,\text{out}} - w_{i,\text{in}}) \dot{m}_{\text{tot}}}{M_i W_{\text{cat}}} \quad (1)$$

## Results and Discussion

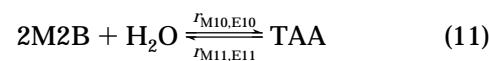
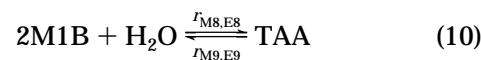
The following main reactions (2–4 and 5–7) were observed in the synthesis of tertiary ethers (set II and set III, respectively):



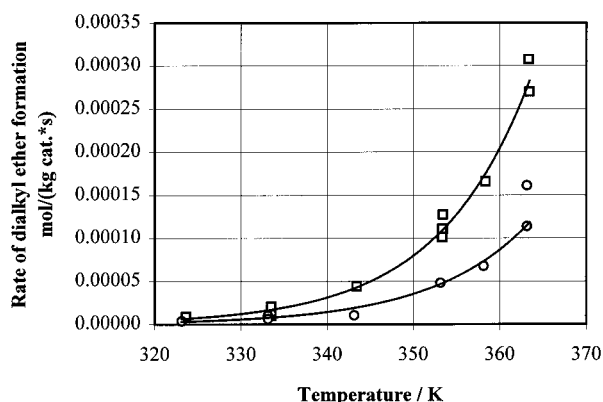
Formation of dialkyl ethers was observed in lower quantities:



The water produced in the dehydration reactions (8 and 9) reacted with isoamylenes to yield *tert*-amyl alcohol (TAA, 2-methyl-2-butanol) (10) and (11):



The amount of possible residual water could not be



**Figure 1.** Rates of dialkyl ether formation vs temperature (set I): (□) DME from MeOH, 23 mol/L and (○) DEE from EtOH, 16 mol/L.

**Table 1. Calculated Thermodynamic Equilibrium Constants and Conversions, and the Obtained Experimental Conversions (Set I) between 323 and 363 K for the Formation of DME from MeOH**

$T$ (K)	$\Delta_r G$ (kJ/mol)	$K$ (thermodyn.)	eq. conv. of MeOH (%)	exp. conv. of MeOH (%)
323.15	-12.1	88.56	94.78	0.04
333.15	-12.0	77.14	94.35	0.07
343.15	-12.0	67.82	93.92	0.21
353.15	-12.0	60.15	93.50	0.62
363.15	-12.0	53.77	93.07	1.49

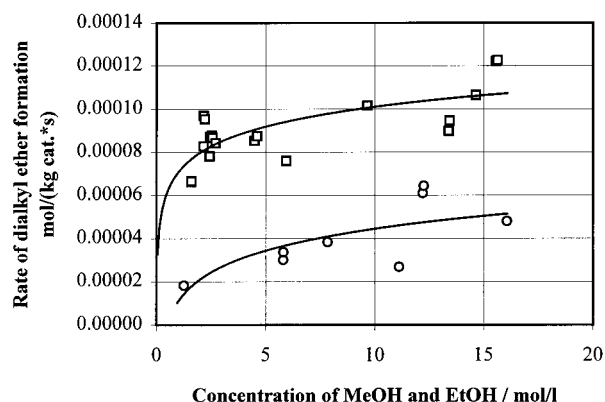
**Table 2. Calculated Thermodynamic Equilibrium Constants and Conversions, and the Obtained Experimental Conversions (Set I) between 323 and 363 K for the Formation of DEE from EtOH**

$T$ (K)	$\Delta_r G$ (kJ/mol)	$K$ (thermodyn.)	eq. conv. of EtOH (%)	exp. conv. of EtOH (%)
323.15	-12.2	94.05	91.17	0.01
333.15	-12.2	82.35	90.71	0.02
343.15	-12.2	72.61	90.25	0.03
353.15	-12.2	64.37	89.79	0.14
363.15	-12.2	57.33	89.33	0.40

measured by GC analysis. However, our calculations based on the stoichiometry of the reaction scheme above indicate that almost all water reacted further in the hydration reactions (10) and (11), producing the tertiary alcohol. No dimerization products were detected in the experiments.

The rates of formation of the dehydration products from pure alcohols (set I) as a function of temperature are presented in Figure 1. The results show the formation of DME and DEE to be favored by higher temperatures. Moreover, the reactions are not thermodynamically controlled within the investigated range. Separate thermodynamical calculations presented in Table 1 (DME) and Table 2 (DEE) also show that the rate of the reverse reaction (splitting of the dialkyl ether) must be negligible since the values of the calculated equilibrium conversions are large relative to the measured conversions of DME and DEE. The values of the thermodynamic equilibrium constants were calculated with the flow sheet program FLOWBAT (Keskinen and Aittamaa, 1996) by applying the Gibbs free energy minimization for equilibrium calculations. The thermodynamic pure component data were obtained from Daubert and Danner (1992).

The dehydration rates of the alcohols cannot be directly compared from Figure 1, because of the different mole specific volumes and consequent concentration



**Figure 2.** Rates of dialkyl ether formation vs alcohol concentration (sets II and III): (□) DME from MeOH and (○) DEE from EtOH. Temperature was 353 K.

**Table 3. Experimental Results of the Kinetic Runs for TAME at 353 K (Set III)**

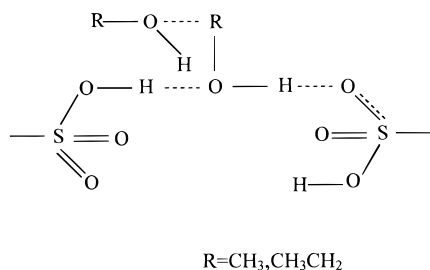
conc. of MeOH (mol/L)	M/IA molar ratio	solvent (wt %)	$r_{\text{DME}} \times 10^5$ (mol/(kg s))	$r_{\text{TAME}}$ (mol/(kg s))	$r_{\text{TAME}}/r_{\text{DME}}$
2.2	1.0	61	9.67	0.020	205
2.2	1.0	61	8.27	0.019	225
2.2	1.0	61	9.53	0.021	224
2.4	1.0	51	8.69	0.024	271
2.7	1.0	52	8.42	0.022	265
2.5	1.0	52	8.76	0.020	230
2.6	1.0	52	8.66	0.020	230
2.4	2.1	73	7.80	0.011	141
4.5	2.2	52	8.51	0.017	200
4.6	2.2	52	8.73	0.018	212
13	9.2	21	8.94	0.015	170
13	9.2	21	9.42	0.015	163

difference. The liquid densities of the product streams were calculated with FLOWBAT by applying the model of Aalto *et al.* (1996). Although the model was originally developed for hydrocarbon mixtures, the authors tested it against liquid density data of alcohol-hydrocarbon mixtures. The average absolute deviation was found to be less than 5%, a level of accuracy adequate for our purposes since the concentrations are used only for qualitative conclusions. The results for experiments where the concentration was varied (set II for MeOH and EtOH; set III for MeOH) at a temperature of 353 K are presented in Figure 2. The figure shows that the dehydration rates of both methanol and ethanol increase with increasing alcohol concentration. A clear difference can be seen between the dehydration rates of methanol and ethanol, with the rate of methanol dehydration being faster. The same difference was observed at 343 K, but at 333 K the dehydration rates were so small that they are undistinguishable.

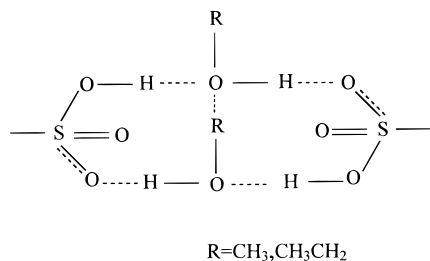
The results of the selectivity studies on TAME (set III) are presented in Table 3. Selectivity was studied by comparing the formation rate of TAME with the formation rate of DME. As the results show, when the reaction is maintained in a kinetic regime, the reaction is highly selective for *tert*-etherification. Although no similar experiments were carried for TAEE, the reaction for *tert*-etherification (TAEE formation) must be highly selective as the dehydration rate of ethanol was even smaller than the dehydration rate of methanol.

#### Kinetic Modeling of DME and DEE Formation.

**Model 1.** The dehydration mechanism could be of the type where one alcohol molecule is adsorbed and the other reacts from the liquid phase (Figure 3). Assuming



**Figure 3.** Mechanism proposed for alcohol dehydration according to model 1: single-site reaction.



**Figure 4.** Mechanism proposed for alcohol dehydration according to model 2: dual-site reaction (Gates and Johanson, 1969).

this, the rate for DME/DEE formation is formulated as follows:

$$r_D = k_7 \theta_A a_A \quad (12)$$

$$\theta_A = K_A a_A \theta_{Sa} \quad (13)$$

$$r_D = k_7 K_A a_A^2 \theta_{Sa} \quad (14)$$

**Model 2.** A second possible model for the dehydration is one in which two molecules of alcohol adsorbed on adjacent sulfonic acid groups react and form a dialkyl ether (Figure 4) (Gates and Johanson, 1969). The formulation is as follows:

$$r_D = k_7 \theta_A \theta_A \quad (15)$$

$$r_D = k_7 K_A^2 a_A^2 \theta_{Sa}^2 \quad (16)$$

In the experiments of set II the applied residence time was so long that the tertiary ethers (TAME and TAEE) were obtained in thermodynamic equilibrium amounts. However, since our purpose was to study the dehydration reactions, the long residence times were necessary in order to obtain reasonable amounts of the dialkyl ethers for quantitative analysis. The formation of TAME and DME, and the formation of TAEE and DEE, were analyzed with models similar to those developed earlier. In the case of the TAME kinetics (Rihko *et al.*, 1997), the fraction of the vacant sites obtains the following form ( $\theta_{DME} \sim 0$ )

$$\theta_{Sa} = \frac{1}{1 + K_M a_M + K_T a_T} \quad (17)$$

The formation rate of DME according to model 1 is

$$r_{DME} = \frac{k_{M7} K_M a_M^2}{1 + K_M a_M + K_T a_T} \quad (18)$$

and according to model 2 is

$$r_{DME} = \frac{k_{M7} K_M^2 a_M^2}{(1 + K_M a_M + K_T a_T)^2} \quad (19)$$

For the TAEE kinetics (Linnekoski *et al.*, 1997), the fraction of the vacant sites obtains the following form ( $\theta_{DEE} \sim 0$ ):

$$\theta_{Sa} = \frac{1}{1 + K_E a_E + K_T a_T + \Sigma(K_{IA} a_{IA})} \quad (20)$$

The formation rate of DEE according to model 1 is

$$r_{DEE} = \frac{k_{E7} K_E a_E^2}{1 + K_E a_E + K_T a_T + \Sigma(K_{IA} a_{IA})} \quad (21)$$

and according to model 2 is

$$r_{DEE} = \frac{k_{E7} K_E^2 a_E^2}{(1 + K_E a_E + K_T a_T + \Sigma(K_{IA} a_{IA}))^2} \quad (22)$$

**Results of Parameter Estimation.** The rate equations for DME and DEE formation were further modified for parameter estimation. Since the practical objective of our study was to expand the previously presented kinetic models to cover the dehydration of the alcohol as a side reaction, we made the same assumptions as in our previous papers (Rihko *et al.*, 1997; Linnekoski *et al.*, 1997). Thus, by dividing eq 18 by  $K_M$ , and assuming that the term  $1/K_M$  is small relative to the other terms in the denominator, we obtain according to model 1 a formation rate for DME in the form

$$r_{DME} = \frac{k_{M7} a_M^2}{a_M + \frac{K_T}{K_M} a_T} \quad (23)$$

Similarly, dividing eq 19 by  $K_M^2$ , we obtain according to model 2 a formation rate for DME in the form

$$r_{DME} = \frac{k_{M7} a_M^2}{\left(a_M + \frac{K_T}{K_M} a_T\right)^2} \quad (24)$$

In a similar manner, the kinetic equations for the formation rate of DEE are simplified by assuming that the adsorption of the strongly polar component (alcohol) is much stronger than the adsorption of the less polar components (isoamylenes and ether). In other words, the terms  $\Sigma(K_{IA} a_{IA})$  and  $K_T a_T$  are considered to be much smaller than the term  $1 + K_E a_E$  in the denominator. The formation rate of DEE according to model 1 then reduces to the form

$$r_{DEE} = \frac{k_{E7} K_E a_E^2}{K_E a_E + 1} \quad (25)$$

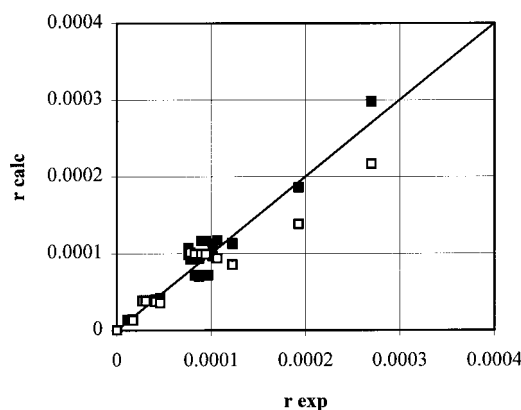
and according to model 2 to the form

$$r_{DEE} = \frac{k_{E7} K_E^2 a_E^2}{(K_E a_E + 1)^2} \quad (26)$$

After these simplifications, it was possible to apply the parameter values  $K_T/K_M$  and  $K_E$  obtained earlier

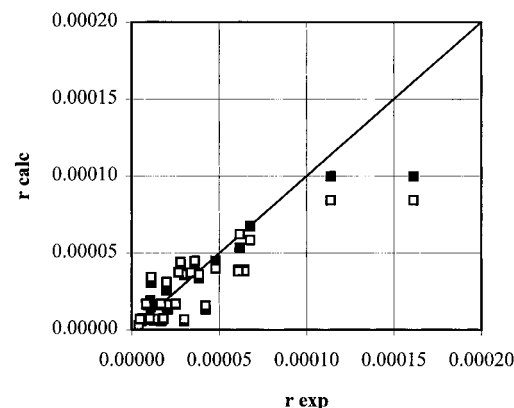
**Table 4. Values of DME and DEE Formation Rate Parameters at 343 K and Their Activation Energies with 95% Confidence Limits According to Model 1 and Model 2 (Standard Error (SE) and Goodness of the Fit ( $R^2$ ))**

	model 1	model 2
$k_{M7}$ (at 343 K) (mol kg <sup>-1</sup> s <sup>-1</sup> )	$4.95 \times 10^{-5}$	$3.92 \times 10^{-5}$
$E_{act,DME}$ (kJ mol <sup>-1</sup> )	$102.6 \pm 9.5$	$95.1 \pm 10.2$
$K_T/K_M$	$=\exp(-10.1253+2912.0/T)$	
SE	0.191 853	0.204 898
$R^2$	0.951 659	0.936 779
$k_{E7}$ (at 343 K) (mol kg <sup>-1</sup> s <sup>-1</sup> )	$2.43 \times 10^{-5}$	$2.88 \times 10^{-5}$
$E_{act,DEE}$ (kJ mol <sup>-1</sup> )	$90.5 \pm 15.3$	$89.9 \pm 18.8$
$K_E$	$=\exp(-5.5834 + 2369.5/T)$	
SE	0.317 178	0.390 214
$R^2$	0.945 802	0.919 205

**Figure 5.** Calculated vs experimental (sets II and III) rates of DME formation: (■) model 1 and (□) model 2.

in conjunction with the TAME and TAE kinetics (Rihko *et al.*, 1997; Linnekoski *et al.*, 1997). In our earlier studies with TAME, the activity coefficients were estimated by the UNIQUAC (Gmehling and Onken, 1977) method. However, expansion of the model required a more generalized approach, and all earlier data for TAME, including the equilibrium, splitting, and synthesis experimental data, were accordingly recalculated by applying the UNIFAC (Fredenslund *et al.*, 1977) method for estimation of the activity coefficients.

The parameter values for DME formation were estimated by linear regression from the correlations  $\ln[r_{DME}/(1/a_M + ((K_T/K_M)(a_T/a_M^2)))]$  vs  $1/T$  (model 1) and  $\ln[r_{DME}/(1 + (K_T/K_M)(a_T/a_M)^2)]$  vs  $1/T$  (model 2). This method gave us an Arrhenius-type temperature dependency for the parameter  $k_{M7}$ . Parameter values were estimated from the data sets II and III because the correlations include the ratio of the adsorption equilibrium constants for TAME and MeOH. Similarly, the temperature dependencies of the parameter  $k_{E7}$  for DEE formation were estimated from the correlations  $\ln[r_{DEE}/(1/a_E + 1/(K_E a_E^2))]$  vs  $1/T$  (model 1) and  $\ln[r_{DEE}/(1 + 1/(K_E a_E)^2)]$  vs  $1/T$  (model 2) from the data set I. The obtained values and some statistical data are presented in Table 4. The statistical results show that for DME formation the correlation ( $R^2$ ) is better with model 1 than with model 2. The standard error (SE) is also smaller with model 1. For DEE formation the correlation is better with model 1 than with model 2, and the standard error is again smaller with model 1. Figures 5 and 6 present the plots of the experimental and calculated rates of dehydration. As seen from the figures, there is some experimental fluctuation, but still the deviation is much more severe with model 2. Moreover, according to Laidler (1987) a Langmuir–Rideal-type mechanism (model 1) is expected if the plot of rate vs concentration

**Figure 6.** Calculated vs experimental (sets I and II) rates of DEE formation: (■) model 1 and (□) model 2.**Table 5. Expanded Kinetic Model for the Synthesis of TAME**

$$r_{TAME} = \frac{k_{M1}(a_M a_{1B} - a_T/K_{M1}) + k_{M3}(a_M a_{2B} - a_T/K_{M2})}{\left(\frac{K_T}{K_M} a_T + a_M\right)}$$

$$r_{1B} = \frac{-k_{M1}(a_M a_{1B} - a_T/K_{M1})}{\left(\frac{K_T}{K_M} a_T + a_M\right)} - k_{M5}(a_{1B} - a_{2B}/K_{M3})$$

$$r_{2B} = \frac{-k_{M3}(a_M a_{2B} - a_T/K_{M2})}{\left(\frac{K_T}{K_M} a_T + a_M\right)} + k_{M5}(a_{1B} - a_{2B}/K_{M3})$$

$$r_M = \frac{-k_{M1}(a_M a_{1B} - a_T/K_{M1}) - k_{M3}(a_M a_{2B} - a_T/K_{M2}) - 2k_{M7}a_M^2}{\left(\frac{K_T}{K_M} a_T + a_M\right)}$$

$$r_{DME} = \frac{k_{M7}a_M^2}{\left(\frac{K_T}{K_M} a_T + a_M\right)}$$

reaches an asymptotic maximum value similar to that presented in Figure 2.

From these results we can assume that, within the experimental range of our study, the alcohol dehydration is better described with a model where one alcohol molecule is adsorbed and the other reacts from the liquid phase. The difference between the dehydration rates of methanol and ethanol can be explained in terms of their differences in polarity. Methanol is a more polar medium than ethanol—the dielectricity constant of methanol being 32.6 and that of ethanol 24.3 (CRC, 1992)—so that methanol has a greater tendency than ethanol to form a hydrogen bond with the sulfonic group. If the reaction were to occur between two adsorbed molecules of alcohol, an alkyl group would need to invert in order to form an alkyl cation and simultaneous proton-donating and -accepting properties would be required of the sulfonic groups (Tejero *et al.*, 1996). Moreover, our experimental results would then be in contradiction with the stability order of carbocations, since the methyl cation ( $CH_3^+$ ) is less stable than the ethyl cation ( $CH_3CH_2^+$ ) (Fessenden and Fessenden, 1990).

The expanded kinetic equations for the synthesis of TAME are presented in Table 5, and the UNIFAC-based parameters for the TAME model are presented in Table 6. Values of the earlier UNIQUAC-based parameters

**Table 6. Values of UNIFAC-Based Parameters for the TAME Model (Earlier UNIQUAC-Based Parameters in Parentheses)**

	$k_f$ (at 343 K) (mol kg <sup>-1</sup> s <sup>-1</sup> )	$E_{act}$ (kJ mol <sup>-1</sup> )
$k_{M1}$	0.065 (0.079)	76.8 (72.6)
$k_{M3}$	0.026 (0.035)	99.7 (94.1)
$k_{M5}$	0.027 (0.030)	81.7 (81.6)
$k_{M7}$	$5.0 \times 10^{-5}$	102.6
$K_{M1}$	$=\exp(-9.4751 + 4382.3/T)$ $(=\exp(-8.3881 + 4041.2/T))$	
$K_{M2}$	$=\exp(-9.1732 + 3520.3/T)$ $(=\exp(-8.2473 + 3225.3/T))$	
$K_{M3}$	$=K_1/K_2$	
$K_T/K_M$	$=\exp(-10.1253 + 2912.0/T)$ $(=\exp(-3.5703 + 537.0/T))$	

**Table 7. Expanded Kinetic Model for the Synthesis of TAEE**

$$r_{TAEE} = \frac{K_{E1}(a_{1B}a_E - a_T/K_{E1}) + K_{E3}(a_{2B}a_E - a_T/K_{E2})}{(1 + K_E a_E)^2}$$

$$r_{1B} = \frac{-K_{E1}(a_{1B}a_E - a_T/K_{E1})}{(1 + K_E a_E)^2} - \frac{K_{E5}(a_{1B} - a_{2B}/K_{E3})}{(1 + K_E a_E)}$$

$$r_{2B} = \frac{-K_{E3}(a_{2B}a_E - a_T/K_{E2})}{(1 + K_E a_E)^2} + \frac{K_{E5}(a_{1B} - a_{2B}/K_{E3})}{(1 + K_E a_E)}$$

$$r_E = \frac{-K_{E1}(a_{1B}a_E - a_T/K_{E1}) - K_{E3}(a_{2B}a_E - a_T/K_{E2})}{(1 + K_E a_E)^2} - \frac{2K_{E7}a_E^2}{(1 + K_E a_E)}$$

$$r_{DEE} = \frac{K_{E7}a_E^2}{(1 + K_E a_E)}$$

**Table 8. Values of UNIFAC-Based Parameters for the TAEE Model**

	$k_f$ (at 343 K) (mol kg <sup>-1</sup> s <sup>-1</sup> )	$E_{act}$ (kJ mol <sup>-1</sup> )
$K_{E1}$	2.15	76.8
$K_{E3}$	0.631	95.9
$K_{E5}$	0.494	72.9
$k_{E7}$	$2.4 \times 10^{-5}$	90.5
$K_{E1}$	$=\exp(-9.7525 + 4214.3/T)$	
$K_{E2}$	$=\exp(-9.1893 + 3256.2/T)$	
$K_{E3}$	$=K_1/K_2$	
$K_E$	$=\exp(-5.5834 + 2369.5/T)$	

for TAME are included in Table 6 in parentheses. The differences between the numerical values of the UNIFAC- and UNIQUAC-based parameters are appreciable. It must be pointed out again how important it is to apply these parameter values in their correct context, i.e., to use the proper method for estimating the activity coefficients when applying the model for reactor modeling. The expanded kinetic model for TAEE as well as the values for the UNIFAC-based parameters are presented in Tables 7 and 8.

In designing a reactor for etherifications, low temperatures are preferred to achieve both high conversions and less formation of byproducts. The high concentration of feed alcohol drives the equilibrium-controlled main reactions to the right, but also increases the formation of the unwanted dialkyl ethers and water. Therefore, the optimum feed alcohol/olefin ratio is near to the stoichiometric ratio. The water produced in dehydration reacts with the olefins to yield tertiary alcohol, which can be blended into the gasoline pool. The right amount (or place) of catalyst in the various reactor schemes can be calculated from the reactor simulations by applying kinetic models of the type presented in this paper.

## Summary

We measured the effects of temperature and alcohol concentration on the dehydration of methanol and ethanol as a side reaction in tertiary ether synthesis (TAME and TAEE). The formation of dialkyl ethers (DME and DEE) was favored by high temperature and high-alcohol concentration. At higher temperatures, dimethyl ether formed at a faster rate than diethyl ether. Within the experimental range studied, alcohol dehydration was best described with a model where one alcohol molecule is adsorbed and the other reacts from the liquid phase. According to calculations the water formed in the dehydration reactions reacted with the isoamylenes yielding *tert*-amyl alcohol (TAA), which can be blended into the gasoline pool. Expanded kinetic models for the synthesis of TAME and TAEE were presented and reactor design was briefly discussed.

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## Notation

$a_i$  = activity of component  $i = \gamma_i x_i$   
 $\Delta_r G$  = reaction Gibbs free energy change, kJ mol<sup>-1</sup>  
 $\Delta_r H$  = reaction enthalpy change, kJ mol<sup>-1</sup>  
 $\Delta_r S$  = reaction entropy change, kJ mol<sup>-1</sup> K<sup>-1</sup>  
 $E_{act}$  = activation energy, kJ mol<sup>-1</sup>  
 $F_i$  = molar flow of component  $i$ , mol s<sup>-1</sup>  
 $m_{tot}$  = total flow, g s<sup>-1</sup>  
 $k_{Aj}$  = rate constant of reaction  $Aj$ ,  $A = M, E$  and  $j = 1-7$ , mol kg<sup>-1</sup> s<sup>-1</sup>  
 $K_i$  = adsorption equilibrium constant for component  $i$   
 $K$  = thermodynamic equilibrium constant  
 $K_{Aj}$  = reaction equilibrium constant for a reaction  $Aj$ ,  $A = M, E$  and  $j = 1-3$   
 $M_i$  = molar mass of the component  $i$ , g mol<sup>-1</sup>  
 $r_i$  = rate of reaction for component  $i$ , mol kg<sup>-1</sup> s<sup>-1</sup>  
 $r_{Aj}$  = rate of reaction  $Aj$ ,  $A = M, E$  and  $j = 1-11$   
 $r_{calc}$  = rate of dehydration calculated by a model, mol kg<sup>-1</sup> s<sup>-1</sup>  
 $r_{exp}$  = rate of dehydration measured experimentally, mol kg<sup>-1</sup> s<sup>-1</sup>  
 $T$  = temperature, K  
 $w_i$  = weight fraction of the component  $i$   
 $W_{cat}$  = catalyst mass, kg  
 $x_i$  = molar fraction of component  $i$

## Abbreviations

2M1B = 2-methyl-1-butene  
 2M2B = 2-methyl-2-butene  
 cat = catalyst, kg  
 DEE = diethyl ether  
 DME = dimethyl ether  
 ETBE = ethyl *tert*-butyl ether, 2-ethoxy-2-methylpropane  
 EtOH = ethanol  
 FCC = fluid catalytic cracking  
 IB = isobutene, 2-methyl-1-propene  
 MeOH = methanol  
 MTBE = methyl *tert*-butyl ether, 2-methoxy-2-methylpropane  
 $R^2$  = regression =  $1 - ((\sum(y_{exp} - y_{est})^2)/(\sum(y_{exp} - \bar{y})^2))$

RVP = Reid vapor pressure

SE = standard error

TAA = *tert*-amyl alcohol, 2-methyl-2-butanol

TAAE = *tert*-amyl ethyl ether, 2-ethoxy-2-methylbutane

TAME = *tert*-amyl methyl ether, 2-methoxy-2-methylbutane

#### Subscripts and Superscripts

A = alcohol (MeOH or EtOH)

D = dialkyl ether (DME or DEE)

DEE = diethyl ether

DME = dimethyl ether

E = ethanol

IA = isoamylenes (2M1B and 2M2B)

M = methanol

Sa = vacant adsorption site

T = tertiary ether (TAME or TAAE)

TAAE = *tert*-amyl ethyl ether

TAME = *tert*-amyl methyl ether

#### Greek Letters

$\gamma$  = activity coefficient of component *i*

$\theta$  = fraction of the surface covered by component *i*

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