APPLIED CHEMISTRY

Reaction Equilibrium in the Isomerization of 2,4,4-Trimethyl Pentenes

Reetta S. Karinen,* Mikko S. Lylykangas, and A. Outi I. Krause

Helsinki University of Technology, Laboratory of Industrial Chemistry, P.O. Box 6100, FIN-02015 HUT, Finland

The isomerization reaction of 2,4,4-trimethyl-1-pentene to 2,4,4-trimethyl-2-pentene was studied. In contrast to the general rule for alkene stability, an excess of the α-alkene (2,4,4-trimethyl-1-pentene) was observed in the thermodynamic equilibrium. The result is explained in terms of the molecular structure: the large and bulky substituents in 2,4,4-trimethyl-2-pentene cause steric tension and make the molecule less stable. A reaction enthalpy of 3.51 ± 0.03 kJ mol^{-1}, i.e., endothermic reaction, and a reaction entropy of -0.47 ± 0.10 J mol^{-1} K^{-1} were determined from the experimental data of the isomerization reaction.
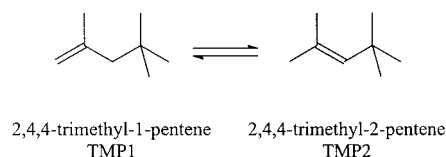
Introduction

The recent troubles concerning MTBE (methyl *tert*-butyl ether, 2-methoxy-2-methyl propane), including a ban on the use of MTBE in some regions,[1] have inspired refiners to seek new uses for isobutene and existing MTBE production facilities to produce high-octane components for gasoline. Two companies have already introduced new process configurations for producing isooctane from isobutene:[2−4] isobutene is first dimerized to isooctene and then hydrogenated to isooctane.

The main dimeric products of isobutene are 2,4,4-trimethyl-1-pentene (TMP1) and 2,4,4-trimethyl-2-pentene (TMP2). In the α-alkene, TMP1, the double bond is attached to the carbon atom at the end of the carbon chain (at the α-carbon), whereas in the β-alkene, TMP2, it is attached to the second carbon from the end of the chain (at the β-carbon). Typically, the equilibrium of alkenes favors the species with the double bond farther from the end of the carbon chain, in order to produce the highest possible substitution of the double bond.[5] This has been demonstrated, e.g., for C_5 and some C_6 and C_8 alkenes, where the β-alkene is thermodynamically favored over the corresponding α form in the range 30−100 °C.[6,7] In our recent study on the etherification of 2,4,4-trimethyl pentenes,[8] the opposite was observed, and this encouraged us to study the isomerization equilibrium further.

It has been reported that the acid-catalyzed polymerization of isobutene produces TMP1 and TMP2 in a ratio of about 4:1[5,9−14], but the thermodynamics for the isomers has not been discussed in detail. Some thermodynamic data have been presented for the enthalpy of formation[15−19] and the standard entropy[16,18−20] of trimethyl pentene molecules, and for the isomerization reaction enthalpy,[21] but the variation within these values is extremely large, e.g., the reaction enthalpy is exothermic in some references and endothermic in

* Corresponding author. E-mail: reetta.karinen@hut.fi. Fax: +358-9-451 2622.

Scheme 1. Reaction scheme of isomerization between TMP1 and TMP2

2,4,4-trimethyl-1-pentene   2,4,4-trimethyl-2-pentene
TMP1   TMP2

others, and the equilibrium data obtained from the literature values are inconsistent. The reaction enthalpy is an important parameter in the modeling and reactor design of the reactions related to 2,4,4-trimethyl pentenes. Especially now, when there is growing interest in the production of gasoline components via these components, accurate thermodynamic data are very important. These trimethyl pentenes are suitable gasoline components as such because of their high octane ratings.[22]

During recent years, trimethyl pentenes have mainly been studied as side products in the etherification of isobutene with alcohols,[23−25] but in addition, the oligomerization of isobutene[26] and simultaneous etherification and isomerization of isobutene[22] has been reported. The formation of excess α-alkene, as well as the faster formation rate of α-alkene, have been reported,[23] but mostly the formation of the two isomers has not been distinguished.

The findings summarized above clearly reveal the confusing situation with regard to the thermodynamics of TMP1 and TMP2. We have now investigated the matter further, and this paper presents thermodynamic data for the isomerization of the trimethyl pentenes (see Scheme 1), studied experimentally and in terms of structure. The isomerization is studied in typical etherification conditions at 50−100 °C but in the absence of alcohols.

Experimental Section

Reactor. The experiments were carried out in a 80-cm^3 stainless steel batch reactor equipped with a

magnetic stirrer and a mixing baffle. The reactor was placed in a water or oil bath with which the temperature of the reactor (50−110 °C) was adjusted. The reaction pressure was maintained at 0.8 MPa with nitrogen to ensure that the reaction mixture remained in the liquid phase. The catalyst, 1−1.5 g, was placed in a metal gauze basket. Samples from the reaction mixture were taken manually via a sample valve at the top of the reactor.

Analytical Methods. Reactor products were analyzed with a Hewlett-Packard 5890 Series II gas chromatograph equipped with a capillary column DB-1 (J&W Scientific; length = 60 m, film thickness = 1.00 μm, diameter = 0.250 mm) and a flame ionization detector. The products were quantified by an internal standard method.

Catalyst. The catalyst was commercial Amberlyst 35Wet (Rohm & Haas), which is a macroreticular, cationic, strongly acidic ion-exchange resin (H^+ 5.2 equiv/kg). Before the experiments, the catalyst was washed with methanol to remove moisture from the pores and thereafter with cyclohexane to remove methanol. Water has to be removed because it reacts readily with alkenes and forms tertiary alcohols. After each experiment, the catalyst was dried, and the mass of the dry catalyst was used in the calculations.

Chemicals. The reagents were 2,4,4-trimethyl-1-pentene (Fluka Chemica AG, >98%) and 2,4,4-trimethyl-2-pentene (Fluka Chemica AG, >98%). Isooctane (Merck, >99.5%) was used as an internal standard for the analysis, and nitrogen (Aga, 99.5%) was used for pressurization of the reactor. Methanol (Riedel-de Haën, >99.8%) and cyclohexane (Merck, >99.5%) were used for washing of the catalyst.

Calculation. The studied isomerization reaction is

$$TMP1 \leftrightarrow TMP2$$

The equilibrium constant can be expressed with the Gibbs free energy change for the reaction, $\Delta_r G$

$$K_a = \exp\left(-\frac{\Delta_r G}{RT}\right) = \exp\left(-\frac{\Delta_r H}{RT} + \frac{\Delta_r S}{R}\right) \quad (1)$$

where $\Delta_r H$ and $\Delta_r S$ are the enthalpy and entropy changes for the reaction, respectively, and R is the universal gas constant (8.314 J mol^{-1} K^{-1}).

$\Delta_r H$ and $\Delta_r S$ are calculated from the enthalpies and entropies of formation of both isomers according to

$$\Delta_r H = \sum (\nu_i \Delta_f H_i) = \Delta_f H_{TMP2} - \Delta_f H_{TMP1} \quad (2)$$

$$\Delta_r S = \sum (\nu_i \Delta_f S_i) = \Delta_f S_{TMP2} - \Delta_f S_{TMP1} \quad (3)$$

where the subscript f denotes the quantity of formation.

The temperature dependence of $\Delta_r H$ and $\Delta_r S$ is expressed with the heat capacities as follows:

$$\Delta_r H = \Delta_r H^\circ + \int_{T_{ref}}^{T} \Delta c_p \, dT \quad (4)$$

$$\Delta_r S = \Delta_r S^\circ + \int_{T_{ref}}^{T} \frac{\Delta c_p}{T} \, dT \quad (5)$$

where Δc_p is the difference between the heat capacities of TMP1 and TMP2.

Equation 1 is linearized to

$$\ln K_a = -\frac{\Delta_r H}{RT} + \frac{\Delta_r S}{R} \quad (6)$$

If the temperature range is small or if the c_p functions of the molecules are close to each other, the integral terms in eqs 4 and 5 can be regarded as negligible, and $\Delta_r H$ and $\Delta_r S$ can be regarded as independent of temperature over the temperature interval.

The equilibrium constants K_a at different temperatures can be calculated with activities a_i from the corresponding equilibrium molar fractions x_i and the activity coefficients γ_i as follows:

$$K_a = \prod a_i^{\nu_i} = \prod x_i^{\nu_i}\gamma_i^{\nu_i} = \frac{x_{TMP2}}{x_{TMP1}}\frac{\gamma_{TMP2}}{\gamma_{TMP1}} = K_x K_y \quad (7)$$

and the equilibrium constant can be expressed in terms of molar fractions K_x as

$$K_x = \prod x_i^{\nu_i} = \frac{x_{TMP2}}{x_{TMP1}} \quad (8)$$

Results

The isomerization reaction (see Scheme 1) was studied with two separate feeds, TMP1 and TMP2, at 50−110 °C. Each experiment was carried out until no further change in composition was observed. At each temperature, the equilibrium constants were calculated for the reaction of TMP1 and TMP2 according to eqs 7 and 8. The final composition of the reaction mixture (see Figure 1 for the experiment at 80 °C) and the equilibrium constants obtained were the same, within experimental error, for the two feeds at each temperature, and thus, the thermodynamic equilibrium constants for this isomerization reaction can be calculated from the results. The equilibrium was established in from 1 to 6 h depending on the reaction temperature.

The experimental values for the equilibrium constants K_x and K_a are presented in Figure 2. The activity coefficients for the calculation of K_a were determined by the UNIFAC method.[27] K_x varies between 0.26 and 0.32 and K_a between 0.26 and 0.31 in the studied temperature range, i.e., K_x is 1.2−1.6% larger than K_a, and the difference increases with temperature. The values of the activity coefficients were slightly larger for TMP1 (average of 1.03) than for TMP2 (average of 1.01), which results in the different values of K_x and K_a given in Figure 2.

The reproducibility of the isomerization results was extremely good. In repeated experiments, the margin of error in the equilibrium coefficient was less than 1%.

The equilibrium constant increased with temperature, which leads to a positive reaction enthalpy and means that the isomerization is an endothermic reaction. When the logarithm of K_a is plotted against the inverse of the temperature according to eq 6, we obtain $\Delta_r H$ from the slope of the curve and $\Delta_r S$ from the intercept. With regression analysis, we obtain

$$\ln K = -421.67\frac{1}{T} - 0.056 \quad (9)$$

and hence $\Delta_r H = 3.51 \pm 0.03$ kJ mol^{-1} and $\Delta_r S = -0.47 \pm 0.10$ J mol^{-1} K^{-1}. The high correlation constant ($R^2 = 0.9995$) speaks for a reliable fitting of the two parameters.
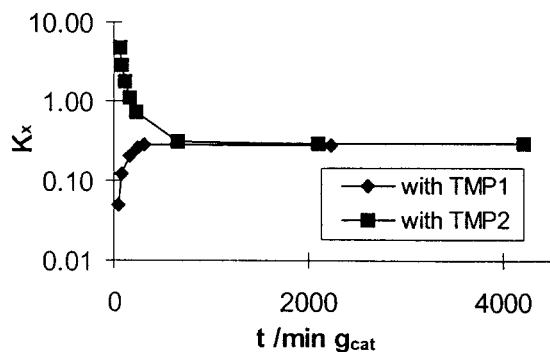
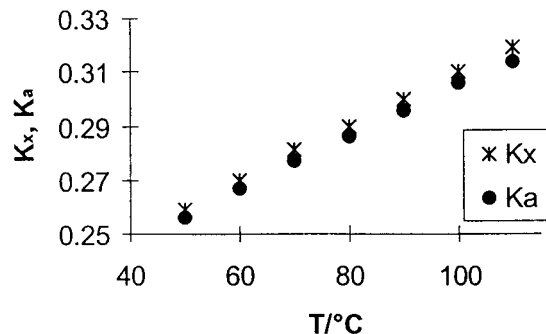**Figure 1.** K_x as a function of contact time in isomerization reactions of TMP1 and TMP2 at 80 °C.

Figure 2. Experimental values of K_x and K_a as a function of temperature.

When the reaction was carried out after equilibrium had been established, isomerization to C_8 alkenes other than TMP1 and TMP2 and oligomerization of the C_8's increased. Thermodynamically some other C_8 isomers, e.g., 2,3,4-trimethyl-1-pentene and 2,3,4-trimethyl-2-pentene, are favored over TMP1 and TMP2 in the gas phase.[28] Although the formation rate of these isomers is low, i.e., the isomerization of the position of the methyl substituent is much slower than the double bond isomerization, new isomers actually appeared with long reaction times (over 1 day). Below 90 °C, the conversion to these species was 1–3%, but the isomerization increased rapidly as the temperature was raised, and at 100–110 °C, conversions of 20–30% were achieved when the reaction time was longer than 1 day. None of the components were identified. Also, oligomers (mainly C_{16} and C_{24}) were detected when the reaction was carried out for a long time. The amounts of these compounds could not be determined.

Thermodynamic Calculations and Estimations. Thermodynamic values for the 2,4,4-trimethyl pentene molecules and the isomerization reaction were gathered from various sources. Table 1 presents values for the standard enthalpies of formation, standard entropies, and standard heat capacities for TMP1 and TMP2 as collected from the literature. The references are separated into two categories according to the type of data: values obtained from experimental results and values calculated by computational estimation methods. Reaction enthalpies calculated from these values range from −11 to 4.6 kJ mol⁻¹. The enthalpies based on experimental data show positive enthalpies of formation and endothermic reactions, which is in agreement with our experimental results. However, the reaction enthalpy value based on estimated thermodynamic values[16] indicated an exothermic reaction.

In addition to gathering data from the literature, we made some estimations of the thermodynamic proper-

ties and equilibrium constants by group contribution methods. All of the reaction enthalpies for the isomerization reaction are gathered in Table 2. With the standard free energy calculated by the Krevelen and Chermin method and the standard heat of formation by the Verma and Doraiswamy method,[29] a reaction enthalpy of −25.3 kJ mol⁻¹ and a K_a value of 3.2 were obtained at 80 °C. In the ideal gas phase, with the thermodynamic properties estimated by the Benson method, a reaction enthalpy of −4.3 kJ mol⁻¹ and a K_a value of 2.5 were obtained at 80 °C.[28] These group contribution methods predict TMP2 to be in excess in the thermodynamic equilibrium. Our experimental results, i.e., reaction enthalpy of 3.5 kJ mol⁻¹ and K_a value of 0.29 at 80 °C and excess of TMP1 in equilibrium, are far from these estimations.

The reaction enthalpy was also calculated by two quantum chemical semiempirical methods, AM1 (Austin method 1) and PM3 (parametrization method 3) methods,[30] and values of 1.78 kJ mol⁻¹ (AM1) and 1.80 kJ mol⁻¹ (PM3)[31] were obtained. AM1 is based on experimental and estimated values, and PM3 is based purely on estimations. The difference in the results of these methods is small, and the most interesting finding is that both AM1 and PM3 predict the isomerization to be an endothermic reaction.

The AM1 and PM3 methods were further tested with a better-known pair of alkene isomers that is similar to 2,4,4-trimethyl pentenes, namely, 2-methyl-1-butene and 2-methyl-2-butene. In this case, both methods indicated an exothermic isomerization reaction (−11.8 to −22.1 kJ mol⁻¹),[32] which also was in accord with experimental results (−6.7 to −8.0 kJ mol⁻¹),[33] although the absolute values differed.

The effect of solvent on the equilibrium composition was studied by simulating the mixture of TMPs in different solvents with the Soave−Redlich−Kwong equation of state. The simulations showed that the ratio of TMP1 to TMP2 in equilibrium was practically independent of the nature and concentration of the solvent. Likewise, elevated pressure was observed to have no effect on the equilibrium. The heat capacities of the two compounds in the studied temperature range were estimated by the method of Rihami and Doraiswamy.[29] Almost identical c_p functions were obtained for the two isomers, which indicates that the reaction enthalpy and entropy are only weakly dependent on the temperature and that the assumptions implicit in eq 6 are therefore justified.

Discussion

A general rule for the stability of alkene isomers is that the more substituted isomer is more stable.[5] Thus, in our case, TMP2, as a trisubstituted alkene, should be more stable than the disubstituted TMP1. Here, however, we encounter an exception to the general rule: the more highly substituted alkene (TMP2) has considerable internal repulsion arising from the large *tert*-butyl group located in the cis position to the methyl group, and the less substituted TMP1 is the major product.

The cause of the internal tension is illustrated as follows. The double bond is rigid and shorter than a single bond. The neighboring atoms form a plane around the double bond, and in the case of TMP1, in addition to the two carbons attached to the double bond, there are two carbon atoms and two hydrogen atoms in the

Table 1. Thermodynamic Properties of TMP1 and TMP2 at 298.15 K

	TMP1			TMP2		
ref[a]	$\Delta_f H^0$ (J mol^{-1})	S_{298}^0 (J K^{-1} mol^{-1})	c_p (J K^{-1} mol^{-1})	$\Delta_f H^0$ (J mol^{-1})	S_{298}^0 (J K^{-1} mol^{-1})	c_p (J K^{-1} mol^{-1})
15, exp	−145.9			−142.4		
17, exp	−147.319			−144.097		
18, exp	−146.1	308.26		−142.4	298.35	
19, exp	−152.130	306.27	236.63[b]	−147.486	311.71	240.11
20, exp					298.7[c]	233.3[c]
16, calc	−152.62	322.58	237.04	−164.58	307.05	258.96

[a] exp = experimental data, calc = calculated by estimation methods. [b] Extrapolated from 296 to 298.15 K with the data of ref 19. [c] According to ref 20, for TMP2, but perhaps actually for the mixture of isomers.

Table 2. Reaction Enthalpies for the Isomerization of TMP1 to TMP2 Obtained from Various Sources

	ref	$\Delta_r H^0$ (kJ mol^{-1})
this work		3.51
literature, based on experiments	15	3.50
	17	3.22
	18	3.70
	19	4.64
	21	5.4
literature, based on estimations	16	−11.96
literature, based on group contribution methods	28	−4.3
	29	−25.3
literature, based on molecular modeling	31	1.78
	31	1.80

plane. In TMP2, three carbon atoms and one hydrogen atom form the plane. TMP2 is trisubstituted and the largest substituent, the *tert*-butyl group, and one methyl group lie on the same side of the double bond, i.e., cis to each other. The *tert*-butyl group is highly branched, and thus, this side of the double bond becomes highly crowded, creating repulsion forces between the *tert*-butyl and methyl substituents. In the case of TMP1, the largest substituent is in the cis position with a hydrogen, which occupies much less space. Also, in TMP1, the bulky *tert*-butyl group is farther away in the position β to the double bond.

The formation of 2,4,4-trimethyl pentenes in an acid-catalyzed dimerization of isobutene has been reported to produce TMP1 and TMP2 in a ratio of 4:1.[5,9−14] It has been explained that, when a protonated isobutene reacts with an isobutene molecule, a C_8 carbocation is formed, where the tertiary carbon has a positive charge. Now, TMP1 is formed in larger amounts because the elimination of a proton takes place more readily from the methyl groups adjacent to the electron-deficient carbon atom than from the neopentyl group. Furthermore, there are six hydrogens attached to the methyl carbons and only two in the methylene group of the neopentyl system.[10] This ratio has also been observed in other reactions related to these alkenes, e.g., in the dehydration of 2,4,4-trimethyl-2-pentanol[34,35] and in the elimination of 2-halo-2,4,4-trimethylpentanes.[21]

The experimental results in the previous section clearly reveal that the thermodynamic equilibrium between TMP1 and TMP2 is an exception to the general rule regarding alkene stability.[5] As seen in Table 2, some of the estimation methods, such as group contribution methods, do not take into account the bulkiness and steric hindrances in the trimethyl pentene molecules and cannot predict the unusual internal steric tension in the TMP2 molecule. These methods suggest an exothermic reaction and an excess of TMP2 at equilibrium, according to the general rule of alkene stability, but these results are in strong contradiction with the experimental data (see Table 1). At the same time, the simulations and estimations show that the more sophisticated and more accurate estimation methods such as molecular modeling methods better take the structure into account and also produce the correct trend for these highly branched molecules.

Conclusions

The isomerization reaction between 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene was studied at 50−110 °C. In the thermodynamic equilibrium composition, 2,4,4-trimethyl-1-pentene, which is the α-alkene, was favored over the β form, which should be the more stable form according to the general rule of alkene stability. This result can be explained in terms of the molecular structure: the more highly substituted β-alkene has strong internal repulsion arising from the large *tert*-butyl substituent next to the double bond, and thus, the molecule is less stable than the α-alkene.

Equilibrium constants for the isomerization reaction were calculated from the experimental results, and these equilibrium constants were used to calculate the reaction enthalpy and reaction entropy. The isomerization reaction was endothermic with a reaction enthalpy of 3.51 kJ mol^{-1} and a reaction entropy of −0.47 J mol^{-1} K^{-1}.

Reaction enthalpy and equilibrium constants were compared with simulated results and data obtained from the literature. Although the variation within the literature values was large, all of the experimental data indicates that the isomerization reaction of TMP1 to TMP2 is an endothermic reaction. It was observed that general estimation methods, such as group contribution methods, cannot predict the thermodynamic properties of the trimethyl pentene molecules correctly, whereas more sophisticated methods, such as quantum chemical calculations, give more reliable results.

Literature Cited

(1) Executive order D-5-99 by the Governor of the State of California, March 25, 1999.

(2) Process converts 'stranded' MTBE units to isooctane. *Eur. Chem. News* **2000**, *72* (1893), 35.

(3) SP isooctane units licensed. *Eur. Chem. News* **2000**, *72* (1894), 39.

(4) Sloan, H. D.; Birkhoff, R.; Gilbert, M. F.; Pyhälahti, A.; Nurminen, M. Isooctane production from C₄'s as an alternative to MTBE. NPRA 2000 Annual Meeting, San Antonio, TX, March 26–28, 2000; AM-00-34.

(5) Solomons, T. W. G. *Organic Chemistry*; John Wiley & Sons Inc.: New York, 1976; pp 221–222.

(6) Rihko, L. K.; Krause, A. O. I. Kinetics of Heterogeneously Catalyzed *tert*-Amyl Methyl Ether Reactions in the Liquid Phase. *Ind. Eng. Chem. Res.* **1995**, *34*, 1172–1180.

(7) Zhang, T.; Jensen, K.; Kitchaiya, P.; Philips, C.; Datta, R. Liquid-Phase Synthesis of Ethanol-Derived Mixed Tertiary Alkyl Ethyl Ethers in an Isothermal Integral Packed-Bed Reactor. *Ind. Eng. Chem. Res.* **1997**, *36*, 4586–4594.

(8) Karinen, R. S.; Krause, A. O. I. Reactivity of some C₈ olefins in etherification with methanol. *Appl. Catal. A* **1999**, *188*, 249–256.

(9) Gallaway, W. S.; Murray, M. J. Isomerization of Certain Olefins by Silica Gel at Room Temperature. *J. Am. Chem. Soc.* **1948**, *70*, 2584–2586.

(10) Schmerling, L.; Ipatieff, V. N. The Mechanism of the Polymerization of Alkenes. *Adv. Catal.* **1950**, *2*, 21–80.

(11) Cram, D. J.; Hammond, G. S. *Organic Chemistry*; McGraw-Hill Inc.: New York, 1959; p 346.

(12) Roberts J. B.; Caserio, M. C. *Modern Organic Chemistry*; W. A. Benjamin, Inc.: New York, 1967; p 154.

(13) Asinger, F. *Mono-Olefins, Chemistry and Technology*; Pergamon Press: Oxford, U.K., 1968; pp 438, 1060.

(14) Zlatkis, A.; Breitmaier, E.; Jung, G. *A Concise Introduction to Organic Chemistry*; McGraw-Hill Kogakusha Ltd.: Tokyo, 1973; pp 74–75.

(15) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermodynamical Data of Organic Compounds*, 2nd ed.; Chapman & Hall: London, 1986; p 97.

(16) Domalski, E. S.; Hearing, E. D. Estimation of the thermodynamic properties of C−H−N−O−S−halogen compounds at 298.15 K. *J. Phys. Chem. Ref. Data* **1993**, *22*, 805–1159.

(17) Rockenfeller, J. D.; Rossini, F. D. Heats of combustion, isomerisation and formation of selected C7, C8 and C10 monoölefin hydrocarbons. *J. Phys. Chem.* **1961**, *65*, 267–272.

(18) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals. Data Compilation*; Hemisphere Publishing Corp.: Washington, D.C., 1992.

(19) Parks, G. S.; Todd, S. S.; Shomate, C. H. Thermal Data on Organic Compounds. XVII. *J. Am. Chem. Soc.* **1936**, *58*, 2505–2508.

(20) Parks, G. S.; Huffman, H. M. Thermal Data on Organic Compounds. IX. *J. Am. Chem. Soc.* **1930**, *52*, 4381–4391.

(21) Turner, R. B.; Nettleton, D. E.; Perelman, M. Heats Of Hydrogenation. VI. Heats of Hydrogenation of Some Substituted Ethylenes. *J. Am. Chem. Soc.* **1958**, *80*, 1430–1433.

(22) Di Girolamo, M.; Lami, M.; Marchionna, M.; Pescarollo, E.; Tagliabue; L.; Ancillotti, F. Liquid-Phase Etherification/Isom-erisation of Isobutene over Sulfonic Acid Resins. *Ind. Eng. Chem. Res.* **1997**, *36*, 4452–4458.

(23) Tejero, J.; Calderón, A.; Cunill, F.; Izquierdo, J. F.; Iborra, M. The formation of byproducts in the reaction of synthesis of isopropyl *tert*-butyl ether from isopropyl alcohol and isobutene on an acidic macroporous copolymer. *React. Funct. Polym.* **1997**, *33*, 201–209.

(24) Rehfinger, A.; Hoffmann, U. Formation of Di-isobutene, Main By-Product of Methyl Tertiary Butyl Ether Synthesis Catalyzed by Ion Exchange Resin. *Chem. Eng. Technol.* **1990**, *13*, 150–156.

(25) Ancillotti, F.; Mauri, M.; Pescarollo, E.; Romangnoni, L. Mechanism in the reaction between olefins and alcohols catalyzed by ion-exchange resins. *J. Mol. Catal.* **1978**, *4*, 37–48.

(26) Haag, W. O. Oligomerisation of isobutylene on cation-exchange resins. *Chem. Eng. Prog. Symp. Ser.* **1967**, *63*, 140–147.

(27) Fredenslund, A.; Gmehling, A.; Rasmussen, P. *Vapour−Liquid Equilibria Using UNIFAC*; Elsevier: New York, 1977; p 380.

(28) Alberty, R. A.; Gehrig, C. A. Standard chemical thermodynamic properties of alkene isomer groups. *J. Phys. Chem. Ref. Data* **1985**, *14*, 803–820.

(29) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977; p 688.

(30) Stewart, J. J. P. MOPAC: A semiempirical molecular orbital program. *J. Comput.-Aided Mol. Des.* **1990**, *4*, 1–105.

(31) Johansson, M.; Ahjopalo, L. VTT Chemical Technology, Research Report KET 751/99; Technical Research Centre of Finland: Espoo, Finland, June 29, 1999.

(32) Johansson, M.; Puhakka, E. VTT Chemical Technology, Research Report KET 788/99; Technical Research Centre of Finland: Espoo, Finland, July 7, 1999.

(33) Rihko, L. K.; Linnekoski, J. A.; Krause, A. O. I. Reaction Equilibria in the Synthesis of 2-Methoxy-2-Methylbutane and 2-Ethoxy-2-Methylbutane in the Liquid Phase. *J. Chem. Eng. Data* **1994**, *39*, 700–704.

(34) Whitmore, F. C.; Rowland, C. S.; Wrenn, S. N.; Kilmer, G. W. Dehydration of Alcohols. XIX. *tert*-Amyl Alcohol and the Related Dimethylneopentylcarbinol. *J. Am. Chem. Soc.* **1942**, *64*, 2970–2972.

(35) Dabbagh, H. A.; Davis, B. H. Catalytic Conversion of Alcohols: Olefin Selectivity from 2,4,4-Trimethyl-2-pentanol using Metal Oxide Catalysts Selective for Hoffmann or Saytzeff Elimination. *J. Mol. Catal.* **1988**, *47*, 123–127.