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Thermochemistry of Branched Ethers: Experimental Study of Chemical Equilibrium in the Reacting System of *tert*-Amyl Alkyl Ether Synthesis

Sergey P. Verevkin*

Department of Physical Chemistry, University of Rostock, Hermannstr. 14, 18051 Rostock, Germany

The chemical equilibrium of the reactive systems (alkanol + methylbutenes ⇔ alkyl *tert*-amyl ether) with the following alkyl substituents: ethyl, propyl, butyl, iso-propyl, *sec*-butyl, and cyclohexyl, were studied in the liquid phase. Reactions were investigated in the screwed vials in the temperature range (298 to 393) K, and a cation exchanger Amberlist 15 was used as heterogeneous catalyst. Enthalpies of reactions $\Delta_r H^\circ_m$ of *tert*-amyl alkyl ethers synthesis in the liquid phase were obtained from the temperature dependence of the equilibrium constants and used to derive standard enthalpies of formation, $\Delta_f H^\circ_m(l)$, of *tert*-amyl alkyl ethers. For the sake of comparison, these enthalpies of formation have been calculated using improved Benson's increments. Calculated values are in close agreement with those from thermochemical measurements.

1. Introduction

tert-Alkyl ethers, namely, methyl *tert*-butyl ether, were introduced in commercial gasoline at the end of 70s, and methyl *tert*-amyl ether was added to gasoline at the end of 90s as a nontoxic octane enhancer to replace lead compounds and to reduce emissions. These branched alkyl ethers are synthesized in an acid-catalyzed equilibrium reaction of olefins (isobutene or isoamylenes) with methanol in the liquid phase.[1−8] Higher ethers (see Figure 1) are synthesized by the reactions with long-chain alcohols. An advantage of high ethers is that they have substantially lower vapor pressure in comparison to methyl *tert*-butyl ether and methyl *tert*-amyl ether and better meet the amendments of the blend Reid vapor pressure (bRvp) levels. Another advantage is that ethyl *tert*-amyl ether (TAEE) is partially produced from a renewable resource, i.e., ethanol. Despite the growing interest in higher ethers, few studies have been published regarding their formation and thermochemistry. Rihko et al.,[3] as well as Datta et al.,[4,5] reported equilibrium constants of the reactions of TAEE synthesis. Linnekoski et al.[6,7] elucidated some kinetic aspects of the methyl *tert*-amyl ether, TAEE, and propyl *tert*-amyl ether synthesis reactions.

In our previous works,[8−12] we developed a procedure to determine the thermodynamic equilibrium constant K_a and $\Delta_r H^\circ_m$ for etherification reactions from experimental data of K_x without measuring activity coefficients γ_i of the reactants. A detailed study of the system

methanol + 2-methyl-2-butene ⇔ methyl *tert*-amyl ether (2-methyl-2-methoxybutane) (1)

has revealed that equilibrium constant K_x (calculated from the mole ratios of the reaction participants) is not equal but essentially close to thermodynamic constant K_a in mixture compositions containing an excess of methanol.[8]

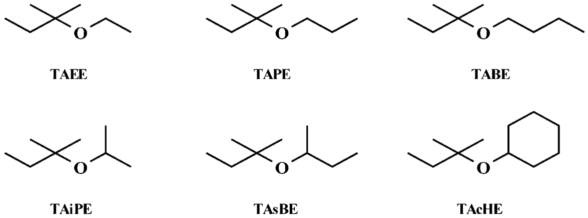

Figure 1. Structures of *tert*-amyl alkyl ethers, involved in the investigation of chemical equilibrium.

Other systems behave similarly leading to the conclusion that the study of ether synthesis reactions equilibrium at compositions with a considerable excess of the alcoholic component allows us to determine K_a without additional measurements of single γ_i values.[8−12] The same procedure is applied now in this work to derive reliable thermodynamic functions of the *tert*-alkyl synthesis reactions in the liquid phase in the temperature range from 298 K to 393 K

ethanol + 2-methylbutene-2 ⇔ ethyl *tert*-amyl ether (2-methyl-2-ethoxybutane) (2)

propanol + 2-methylbutene-2 ⇔ propyl *tert*-amyl ether (2-methyl-2-propoxybutane) (3)

butanol + 2-methylbutene-2 ⇔ butyl *tert*-amyl ether (2-methyl-2-butoxybutane) (4)

2-propanol + 2-methylbutene-2 ⇔ isopropyl *tert*-amyl ether (2-methyl-2-isopropoxybutane) (5)

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* To whom correspondence should be addressed. E-mail: sergey.verevkin@chemie.uni-rostock.de.

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sec-butanol +
2-methylbutene-2 ⇔ *sec*-butyl *tert*-amyl ether
(2-methyl-2-*sec*-butoxybutane) (6)

cyclohexanol +
2-methylbutene-2 ⇔ cyclohexyl *tert*-amyl ether
(2-methyl-2-cyclohexyloxybutane) (7)

We reported just recently the improved Benson's group additivity increments to estimate the standard enthalpies of formation as well as standard enthalpies of vaporization of alkyl ethers, acetals, ketals, and ortho esters.[13] There it has been revealed that, because of the scarce basis of experimental data, the number of additive parameters, such as a tertiary C−(O)(C)2(H) or a quaternary C−(O)(C)3 carbon atom attached to a functional group (O) have been evaluated only from the data for one or two branched ethers. These parameters have to be checked for their validity. For this purpose, the enthalpies of reactions 2−7 of *tert*-amyl alkyl ethers synthesis in the liquid phase were obtained from the temperature dependence of the equilibrium constants and used to derive standard enthalpies of formation, $\Delta_f H^\circ_m(l)$, of *tert*-amyl alkyl ethers. Comparison of these experimental enthalpies of formation with those calculated by improved Benson's increments should be a valuable test of their validity.

2. Experimental Section

Materials. All alcohols were of commercial origin (Aldrich and Fluka). GC analyses of the as-purchased samples gave a purity >99.9%, in agreement with their specifications. A technical fraction of isoamylenes (methylbutenes) with the mass percentages: hydrocarbons C_4, 1.9; 2-methylbutene-1 (2MB1), 39.6; 2-methylbutene-2 (2MB2), 56.0; and 3-methylbutene-1 (3MB1), 2.5, were used in the experiments. *tert*-Amyl alkyl ethers were synthesized via alkylation of an appropriate alkanol with the fraction of methylbutenes in the presence of a catalytic amount of cation-exchange resin in H^+ form (Amberlist 15, Aldrich) at 343 K. Prior to the experiments, the catalyst was dried 8 h at 383 K in a vacuum oven at reduced pressure. Pure samples (99.9 mass %) of *tert*-amyl alkyl ethers (Figure 1) were obtained by repeated distillations at reduced pressure and their structures were confirmed by NMR analysis

Chemical Equilibrium Study in the Liquid Phase. Glass vials with screwed caps were filled two-thirds full with the initial liquid mixture of alkanol and isoamylenes. Cation-exchange resin Amberlist 15 was added as a solid catalyst. The quantity of catalyst was approximately 10% from the mass 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 the vial was then preceded 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 determined chromatographically with a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame-ionization detector. A capillary column HP-5 (stationary phase cross linked 5% PH ME silicone) was used with a column length of 30 m, an inside diameter of 0.32 mm, and a film thickness of 0.25 μm. Response factors of all reagents were determined using calibration mixtures of the corresponding components prepared gravimetrically. Accuracy of the GC analysis of the liquid-phase composition estimated to be within ±0.0005 mass %. The equilibrium ratios K_x of reactions 2−7 were calculated with the help of mole fractions x_i of reaction participants

$$K_x = x_{(ether)}/x_{(ROH)} \cdot x_{(2MB2)} \qquad (8)$$

Mole fractions at equilibrium in the liquid x_i and the thermodynamic equilibrium constants in the liquid phase K_x are listed in Tables 1−6.

Table 1. Results from the Liquid-Phase Investigation of Equilibrium of the Ethyl *tert*-Amyl Ether (TAEE) Synthesis Reaction[a]

		mole fractions					
T/K	n	x_{EtOH}	x_{MB}	x_{2MB2}	x_{tAmOH}	x_{TAEE}	$K_x(2)$
298.2	12	0.0714	0.0878	0.2840		0.5567	27.5[b]
	10	0.4739	0.0328	0.0689	0.0171	0.4073	12.5[b]
	8	0.5518	0.0512	0.0601	0.0128	0.3241	9.8
	8	0.7932	0.0226	0.0201	0.0125	0.1516	9.5
	7	0.9057	0.0067	0.0080	0.0092	0.0704	9.8
313.2	11	0.0882	0.1071	0.3419		0.4628	15.3[b]
	8	0.3894	0.0707	0.1764	0.0090	0.3545	5.2
	10	0.5637	0.0534	0.0871	0.0250	0.2707	5.5
333.2	8	0.1561	0.1255	0.3720		0.3464	6.0[b]
	9	0.3365	0.1062	0.2711	0.0060	0.2803	3.1
	7	0.6296	0.0430	0.1067	0.0186	0.2021	3.0
353.2	8	0.3958	0.0947	0.2640	0.0119	0.2336	2.24[b]
	7	0.6278	0.0529	0.1464	0.0215	0.1464	1.65
	8	0.7879	0.0277	0.0699	0.0240	0.0905	1.64
373.2	7	0.3926	0.0775	0.3684	0.0072	0.1542	1.06
	8	0.6180	0.0645	0.1893	0.0091	0.1191	1.02
393.2	6	0.3534	0.1323	0.3846	0.0076	0.1221	0.90[b]
	6	0.5935	0.0817	0.2313	0.0068	0.0866	0.63

[a] Experimentally determined composition of equilibrium mixtures and K_x values in the liquid phase, calculated from eq 8. (T is temperature of investigation, n is number of determinations of composition within the time of equilibrium study, and x_i is the mole fraction measured chromatographically.) [b] Value was not taken into account by calculation of the thermodynamic functions of reaction 2.

Table 2. Results from the Liquid-Phase Investigation of Equilibrium of the Propyl *tert*-Amyl Ether (TAPE) Synthesis Reaction[a]

		mole fractions					
T/K	n	x_{PrOH}	x_{MB}	x_{2MB2}	x_{tAmOH}	x_{TAPE}	$K_x(3)$
298.2	6	0.0377	0.1081	0.2791		0.5752	54.7[b]
	7	0.3562	0.0683	0.0974	0.0146	0.4635	13.4[b]
	5	0.5036	0.0378	0.0640	0.0133	0.3813	11.8
	7	0.5666	0.0409	0.0538	0.0127	0.3259	10.7
	8	0.6838	0.0235	0.0332	0.0141	0.2454	10.8
	7	0.8336	0.0085	0.0135	0.0119	0.1326	11.8
	7	0.9074	0.0052	0.0071	0.0076	0.0727	11.2
313.2	5	0.0490	0.1058	0.3117		0.5335	34.9[b]
	6	0.3526	0.0753	0.1363	0.0107	0.4251	8.8[b]
	7	0.6121	0.0432	0.0738	0.0146	0.2563	5.7
333.2	8	0.3589	0.0987	0.2411	0.0102	0.2911	3.36[b]
	6	0.8301	0.0226	0.0327	0.0350	0.0796	2.93
	7	0.8803	0.0157	0.0264	0.0092	0.0683	2.94
353.2	8	0.3945	0.0864	0.2458	0.0123	0.2610	2.69[b]
	6	0.6673	0.0435	0.1235	0.0106	0.1552	1.88
	6	0.8786	0.0112	0.0403	0.0078	0.0622	1.76
373.2	7	0.4425	0.0890	0.2833	0.0129	0.1722	1.37[b]
	8	0.7547	0.0381	0.1124	0.0081	0.0868	1.02
393.2	7	0.3907	0.1100	0.3608	0.0087	0.1298	0.92[b]
	8	0.6903	0.0521	0.1661	0.0082	0.0833	0.73

[a] Experimentally determined composition of equilibrium mixtures and K_x values in the liquid phase, calculated from eq 8. (T is temperature of investigation, n is number of determinations of composition within the time of equilibrium study, and x_i is the mole fraction measured chromatographically.) [b] Value was not taken into account by calculation of the thermodynamic functions of reaction 3.

3. Results and Discussion

It was obvious from our results presented in Figures 2 and 3 that reactive mixtures of the *tert*-amyl alkyl ethers

Table 3. Results from the Liquid-Phase Investigation of Equilibrium of the Butyl *tert*-Amyl Ether (TABE) Synthesis Reaction[a]

		mole fractions				
T/K	n	x_{BuOH}	x_{MB}	x_{2MB2}	x_{TABE}	$K_x(4)$
298.2	8	0.0527	0.1607	0.2679	0.5187	36.7[b]
	7	0.4348	0.0733	0.0642	0.4276	15.3[b]
	6	0.6886	0.0420	0.0287	0.2407	12.2
	6	0.7652	0.0195	0.0470	0.1683	12.0
	7	0.8051	0.0279	0.0158	0.1512	11.9
	6	0.8556	0.0241	0.0105	0.1097	12.2
	5	0.9465	0.0059	0.0038	0.0439	12.2
313.2	6	0.1152	0.1071	0.3019	0.4758	13.7[b]
	8	0.3022	0.0986	0.1644	0.4348	8.75[b]
	7	0.6167	0.0627	0.0594	0.2566	7.00
333.2	5	0.0955	0.1385	0.3985	0.3702	9.79[b]
	6	0.6149	0.0319	0.1079	0.2454	3.70
	8	0.6292	0.0511	0.1022	0.2175	3.38
353.2	8	0.3619	0.0965	0.2756	0.2660	2.67[b]
	7	0.6078	0.0560	0.1601	0.1761	1.81
	6	0.7842	0.0526	0.0616	0.1016	2.10
373.2	6	0.4360	0.0897	0.2803	0.1940	1.59[b]
	6	0.7480	0.0507	0.1060	0.0952	1.20
393.2	8	0.4422	0.0959	0.3094	0.1525	1.12[b]
	8	0.7358	0.0281	0.1486	0.0875	0.80

[a] Experimentally determined composition of equilibrium mixtures and K_x values in the liquid phase, calculated from eq 8. (T is temperature of investigation, n is number of determinations of composition within the time of equilibrium study, x_i is the mole fraction measured chromatographically.) [b] Value was not taken into account by calculation of the thermodynamic functions of reaction 4.

Table 4. Results from the Liquid-Phase Investigation of Equilibrium of the Isopropyl *tert*-Amyl Ether (TAiPE) Synthesis Reaction[a]

		mole fractions				
T/K	n	x_{iPrOH}	x_{MB}	x_{2MB2}	x_{TAiPE}	$K_x(5)$
298.2	6	0.1426	0.2965	0.4942	0.0666	0.945[b]
	7	0.4174	0.1969	0.3282	0.0575	0.420[b]
	8	0.7057	0.0691	0.1951	0.0301	0.219
	5	0.8344	0.0407	0.1051	0.0198	0.226
313.2	6	0.8508	0.0069	0.1246	0.0178	0.167
	8	0.8971	0.0048	0.0865	0.0116	0.150
333.2	7	0.7727	0.0719	0.1437	0.0118	0.106
	6	0.8336	0.0522	0.1044	0.0098	0.113
353.2	7	0.7811	0.0540	0.1542	0.0107	0.089
	6	0.8419	0.0391	0.1117	0.0073	0.078
373.2	5	0.4651	0.1266	0.3956	0.0127	0.069
	8	0.7206	0.0657	0.2054	0.0083	0.056

[a] Experimentally determined composition of equilibrium mixtures and K_x values in the liquid phase, calculated from eq 8. (T is temperature of investigation, n is number of determinations of composition within the time of equilibrium study, x_i is the mole fraction measured chromatographically.) [b] Value was not taken into account by calculation of the thermodynamic functions of reaction 5.

Table 5. Results from the Liquid-Phase Investigation of Equilibrium of the *sec*-butyl *tert*-Amyl Ether (TAsBE) Synthesis Reaction[a]

		mole fractions					
T/K	n	x_{sBuOH}	x_{MB}	x_{2MB2}	x_{tAmOH}	x_{TAsBE}	$K_x(6)$
298.2	6	0.2843	0.2283	0.3806	0.0191	0.0872	0.806[b]
	8	0.5117	0.1468	0.2447	0.0258	0.0710	0.567[b]
	6	0.7680	0.0180	0.1526	0.0280	0.0334	0.285
	7	0.8577	0.0081	0.0881	0.0243	0.0219	0.290
	5	0.8962	0.0054	0.0508	0.0343	0.0132	0.290
313.2	6	0.3115	0.2152	0.3912	0.0198	0.0622	0.510[b]
	6	0.4701	0.1608	0.2923	0.0224	0.0544	0.396[b]
	5	0.6686	0.0366	0.2337	0.0284	0.0328	0.210
333.2	6	0.2455	0.2155	0.4789	0.0170	0.0431	0.367[b]
	7	0.4760	0.1433	0.3185	0.0282	0.0341	0.225[b]
	8	0.6678	0.0367	0.2337	0.0386	0.0231	0.148
353.2	6	0.5328	0.1090	0.3116	0.0264	0.0202	0.122
	8	0.6557	0.0789	0.2255	0.0248	0.0151	0.102
	5	0.7998	0.0439	0.1256	0.0215	0.0093	0.093
373.2	5	0.5351	0.1111	0.3176	0.0229	0.0133	0.078
	6	0.7755	0.0714	0.1258	0.0190	0.0082	0.084
393.2	7	0.4532	0.1141	0.4006	0.0203	0.0118	0.064

[a] Experimentally determined composition of equilibrium mixtures and K_x values in the liquid phase, calculated from eq 8. (T is temperature of investigation, n is number of determinations of composition within the time of equilibrium study, x_i is the mole fraction measured chromatographically.) [b] Value was not taken into account by calculation of the thermodynamic functions of reaction 6.

Table 6. Results from the Liquid-Phase Investigation of Equilibrium of the Cyclohexyl *tert*-Amyl Ether (TAcHE) Synthesis Reaction[a]

		mole fractions					
T/K	n	x_{cHexOH}	x_{MB}	x_{2MB2}	$x_{cyclohexen}$	x_{TAcHE}	$K_x(7)$
	7	0.2816	0.2296	0.3826		0.1062	0.986[b]
	8	0.4154	0.1806	0.3010		0.0883	0.824[b]
	7	0.4686	0.1804	0.2776		0.0734	0.564
	6	0.7601	0.0578	0.1282		0.0538	0.552
	8	0.8990	0.0240	0.0518		0.0253	0.543
313.2	6	0.2796	0.2127	0.4255		0.0822	0.691[b]
	5	0.4299	0.0644	0.4323		0.0734	0.395
	8	0.6701	0.0694	0.2049		0.0556	0.405
333.2	6	0.3760	0.1888	0.3776		0.0576	0.406[b]
	8	0.5087	0.0431	0.3918		0.0564	0.283
	7	0.6320	0.0623	0.2596		0.0461	0.281
353.2	5	0.3186	0.1682	0.4806		0.0326	0.213
	6	0.4595	0.1316	0.3759		0.0330	0.191
	8	0.5869	0.0985	0.2813		0.0333	0.202
373.2	7	0.4144	0.1208	0.3777	0.0617	0.0254	0.162
	8	0.6043	0.0800	0.2500	0.0412	0.0244	0.162
393.2	8	0.3737	0.1154	0.3848	0.0970	0.0149	0.104[b]

[a] Experimentally determined composition of equilibrium mixtures and K_x values in the liquid phase, calculated from eq 8. (T is temperature of investigation, n is number of determinations of composition within the time of equilibrium study, x_i is the mole fraction measured chromatographically.) [b] Value was not taken into account by calculation of the thermodynamic functions of reaction 7.

synthesis behave strongly nonideally, especially when the mole fractions of alkanol are low. On that basis, the activity coefficients γ_i should be used to calculate the true thermodynamic equilibrium constant K_a, in the similar way as it was done by Rihko et al.[3] and Datta et al.[4,5] We have studied the equilibrium of reaction of methyl *tert*-amyl synthesis (reaction 1) in the liquid and in the gaseous phases recently.[8] In this work, we tested the ability of two common methods, UNIFAC and COSMO-RS, to predict values of activity coefficients γ_i. The results of this test were disappointing; both methods failed to calculate activity coefficients accurately. However, in our previous works,[8−12] we developed a procedure to determine $\Delta_r H_m^\circ$ for etherification reactions from experimental data of K_x without measuring activity coefficients γ_i of the reactants. Figures 2 and 3 show K_x as a function of the alkanol fraction at 298 K. It is apparent that K_x values are almost independent of the mole fraction of methanol if $x_{ROH} > 0.5$. Taking into account the assumption that the enthalpy of reaction obtained from the temperature dependence of K_x measured above $x_{ROH} > 0.5$ providing the standard enthalpy of reaction $\Delta_r H_m^\circ(l)$ correctly,[8−12] the latter experimental values of K_x were approximated as a function of temperature by the linear equation $\ln K_x\ (x_{ROH} > 0.5) = a + b(T/K)^{-1}$ using the method of least squares. The slope of this line when multiplied by the gas constant yields the

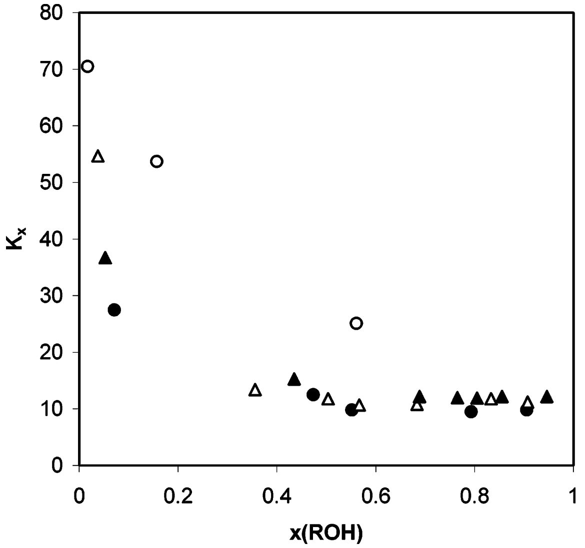

Figure 2. Concentration equilibrium constants K_x of reactions 1−4 as a function of alcohol mol fraction x in the equilibrium mixture at T = 298 K. ○, methanol; ●, ethanol; △, propanol; ▲, butanol.

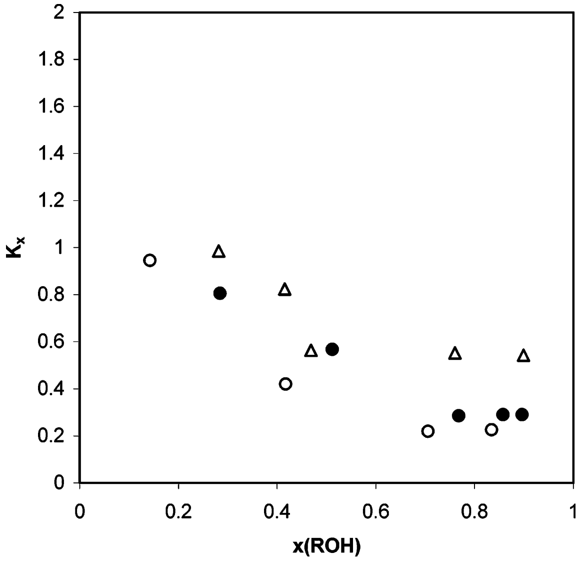

Figure 3. Concentration equilibrium constants K_x of reactions 5−7 as a function of alcohol mol fraction x in the equilibrium mixture at T = 298 K. ○, 2-propanol; ●, *sec*-butanol; △, cyclohexanol.

enthalpy of reaction, $\Delta_r H_m^\circ$, of *tert*-amyl alkyl ether synthesis reactions 2−7. Numerical results are presented in Table 7. The errors in the thermodynamic functions from the equilibrium study are given by the standard deviations for the meaningful level 0.05.

The experimental values of K_x of the reaction 2 measured above $x_{\mathrm{EtOH}} > 0.5$ in this work are in very close agreement (see Figure 3) with those obtained also in excess of ethanol by Rihko et al.[3] Equilibrium constants K_x of the reaction 2, reported by Kitchaiya and Datta,[4] were measured in the range $x_{\mathrm{EtOH}} \approx 0.2-0.3$, and they are in apparent disagreement (see Figure 3) with the equilibrium constants for reaction 2 from this work; however, it is worth mentioning that the trend of their temperature dependence is very similar to the trend of the thermodynamic constants derived in this work.

Table 7. Enthalpy of Reaction $\Delta_r H_m^\circ$ of the Alkyl *tert*-Amyl Ether Synthesis Reactions in the Liquid Phase at T = 298.15 K and Coefficients a and b of the Temperature Dependence of the Equilibrium Constants $\ln K_x = a + b(T/\mathrm{K})^{-1}$

reaction	$\langle T\rangle^a$/K	$\Delta_r H_m^{\circ\,b}$/kJ·mol^{-1}	a	b
1^c	357.1	−28.1 ± 0.6	3383.0	−8.10
2	345.7	−27.7 ± 0.8	3330.0	−8.91
3	345.7	−27.9 ± 1.9	3359.9	−8.93
4	345.7	−28.1 ± 0.8	3384.5	−8.87
5	335.7	−15.5 ± 0.7	1860.1	−7.76
6	345.7	−15.5 ± 0.3	1860.9	−7.50
7	345.7	−15.3 ± 0.8	1837.9	−6.77

[a] The average temperature of the equilibrium study. [b] Derived from the temperature dependence of K_x for $x_{\mathrm{ROH}} > 0.5$. [c] Results from our previous work.[8]

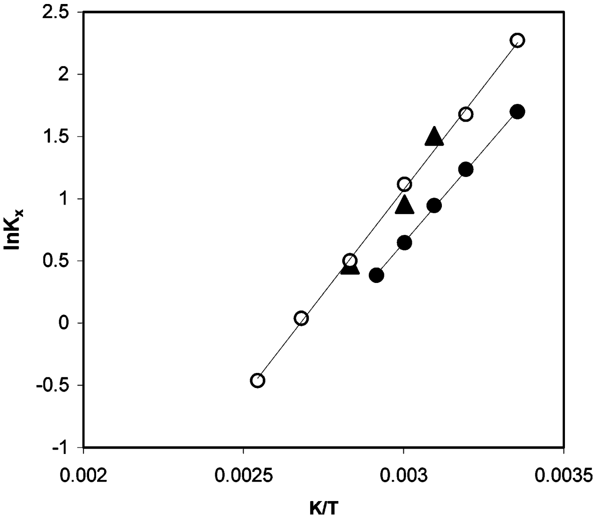

Figure 4. Concentration equilibrium constants K_x of reaction 2 at mol fraction $x_{\mathrm{ethanol}} > 0.5$ as a function of temperature and comparison with some results available from the literature. ●, Kitchaiya and Datta, 1995; ▲, Rihko et al., 1994; ○, this work.

In the experimental works published on the TAEE synthesis reaction, the initial ratio of reactants methanol/methylbutenes was close to the unity.[3,4] Thus, for the thermodynamic interpretation of the equilibrium constants, activity coefficients γ_i of the reaction participants responsible for intermolecular interactions should be taken into account. For this purpose UNIFAC method have been applied,[3,4] and the enthalpies of reaction 2 derived in this way are as follows: $\Delta_r H_m^\circ(2) = (-27.3 \pm 6.7)$ kJ·mol^{-1} by Rihko et al.[3] and $\Delta_r H_m^\circ(2) = -24.3$ kJ·mol^{-1} by Kitchaiya and Datta,[4] and these values are still in acceptable agreement with our value (see Table 7).

For all three systems containing linear alcohols (ethanol, propanol, and butanol), a plot of ln K_x as function of $1/T$ gives straight lines, which are almost parallel to those of methyl *tert*-amyl ether synthesis (see Figure 4); it means that values of enthalpies of reactions 1−4 are expected to be very close. Three other systems (Figure 5) containing branched alcohols (2-propanol, *sec*-butanol, and cyclohexanol) are also parallel to each other.

The chemical equilibrium of the reactive systems of *tert*-amyl ether synthesis was studied in the liquid phase in the temperature range (298 to 393) K. Although equilibrium studies have been performed at elevated temperatures, the corrections of the enthalpies of reactions 2−7 are assessed to be less than (0.3 to 0.5) kJ·mol^{-1} according to our estimations with help of heat capacities of the reaction participants collected in the database.[14] In further calculations, it was assumed that the enthalpies of reactions 2−7 hardly change on passing from the average temperature of the experimental range to T = 298.15 K.

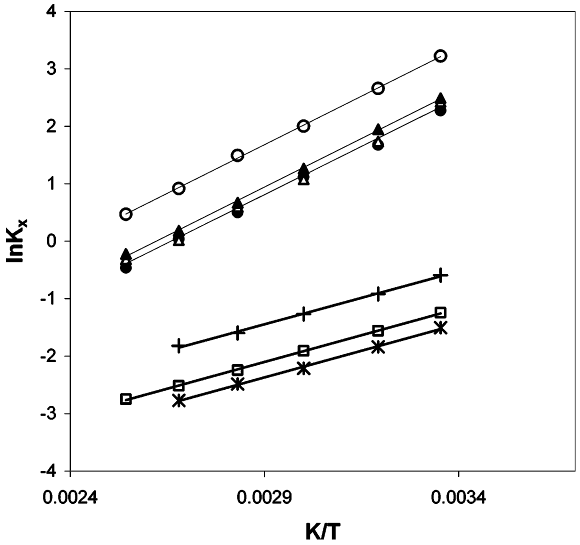

Figure 5. Equilibrium constants K_x for $x_{ROH} > 0.5$ of reactions 1−7 as a function of temperature. ○, methanol; ●, ethanol; △, propanol; ▲, butanol; □, 2-propanol; *, *sec*-butanol; +, cyclohexanol.

When using ion-exchange resins as the catalyst, only tertiary olefins react in the etherification reaction.[15] From the three methylbutenes, 2-methylbutene-1 reacts fastest, and 2-methylbutene-2 reacts 2−5 times slower depending on the alcohol, whereas 3-methylbutene-1 gives no reaction.[15] In addition to the etherification, isomerization of the double bond occurs simultaneously

$$\text{2-methylbutene-1} \Leftrightarrow \text{2-methylbutene-2} \qquad (9)$$

and the equilibrium favors more stable 2-methylbutene-2.[15] Indeed, in our previous work, we studied the chemical equilibrium of reaction 9 simultaneously with the methyl *tert*-amyl ether synthesis reaction 1.[8] In those works, we established that equilibrium constants K_x of reaction 9 were independent of the composition of the equilibrium mixtures and that both reactions 1 and 9 reach equilibrium simultaneously. In those works, we used a mixture of 2-methylbutene-1 and 2-methylbutene-2 (purchased by Merck) instead of a technical fraction of isoamylenes, which has been applied in this work. As a consequence, some impurities of hydrocarbons C_4 were present in the technical fraction and they are eluted together with the peak of 2-methylbutene-1 during the GC analysis following the proper calculation of the equilibrium constant for the isomerization reaction 9 was thwarted. That is why in Tables 1−6 the mole fraction x_{MB} denotes the sum of the 2-methylbutene-1 and residual hydrocarbons C_4 in the equilibrium mixture and why no thermodynamic calculations for reaction 9 have been performed in the reactive systems studied. But because of our earlier observation,[8] that etherification and isomerization reactions reach equilibrium simultaneously, insufficient separation of 2-methylbutene-1 during the GC analysis had no impact on the interpretation of the etherification reactions 2−7.

Enthalpies of reactions 2−7 derived in this work from the temperature dependencies of equilibrium constants (see Table 7) were involved in the calculation of the standard enthalpies of formation of the *tert*-amyl alkyl ethers. For this purpose, standard molar enthalpies of formation, $\Delta_f H^\circ_m$(l), of 2-methylbutene-2 and of alkanols are required. Enthalpy of formation in the liquid phase of 2-methylbutene-2, $\Delta_f H^\circ_m(l) = (-68.1 \pm 1.3)$ kJ·mol^{-1}, was taken from combustion experiments.[16] Further experimental data are also available in the literature: for ethanol, $\Delta_f H^\circ_m(l) = (-277.0 \pm 0.3)$ kJ·mol^{-1}; for 2-propanol, $\Delta_f H^\circ_m(l) = (-317.0 \pm 0.3)$ kJ·mol^{-1}; for *sec*-butanol, $\Delta_f H^\circ_m(l) = (-342.7 \pm 0.6)$ kJ·mol^{-1} were taken from Chao et al.[17] Data for propanol $\Delta_f H^\circ_m(l) = (-302.5 \pm 0.2)$ kJ·mol^{-1} and for butanol $\Delta_f H^\circ_m(l) = (-327.0 \pm 0.2)$ kJ·mol^{-1} were taken from Mosselman and Dekker.[18] Data for cyclohexanol, $\Delta_f H^\circ_m(l) = (-347.4 \pm 2.2)$ kJ·mol^{-1}, were taken from Seller and Sunner.[19] These data together with the enthalpies of reactions 2−7 were used to calculate standard enthalpies of formation of the *tert*-amyl alkyl ethers in the liquid phase (e.g., for *tert*-amyl ethyl ether)

$$\Delta_f H^\circ_{m(\text{liq, TAEE})} = \Delta_r H^\circ_{m(\text{liq, 2})} + \Delta_f H^\circ_{m(\text{liq, EtOH})} + \Delta_f H^\circ_{m(\text{liq, 2MB2})} = -(372.8 \pm 1.6)\ \text{kJ·mol}^{-1}$$

The experimental values obtained of enthalpies of formation derived in this way are given in the Table 8.

Table 8. Comparison of the Standard Molar Enthalpies of Formation $\Delta_f H^\circ_m$(l) of *tert*-Alkyl Ethers Derived from Enthalpies of Reactions 1−7 with Those Calculated by Improved Benson's Scheme[13] at $T = 298.15$ K

compound	abbrev	$\Delta_f H^\circ_m$(l) (exp)/kJ·mol^{-1}	$\Delta_f H^\circ_m$(l) (Benson)[13]/ kJ·mol^{-1}
tert-amyl ethyl ether	TAEE	−372.8 ± 1.6	−373.0
tert-amyl propyl ether	TAPE	−398.5 ± 2.3	−398.5
tert-amyl butyl ether	TABE	−423.3 ± 1.5	−424.1
tert-amyl iso-propyl ether	TAiPE	−400.6 ± 1.5	−400.1
tert-amyl *sec*-butyl ether	TAsBE	−426.3 ± 1.5	−425.6
tert-amyl cyclohexyl ether	TAcHE	−430.8 ± 2.7	−430.6

We reported recently the improved Benson's group additivity increments to estimate the standard enthalpies of formation alkyl ethers.[13] We have applied these increments for the calculation of the branched ethers studied in this work (see Table 8). The calculated values of the $\Delta_f H^\circ_m$(l) are in very close agreement with those derived in this work from chemical equilibrium studies. Such close agreement is a valuable test to establish validity of group additivty increments suggested earlier.[13]

In this work, we performed study of the etherification reactions of linear and branched alcohols with 2-methylbutene-2 systematically and obtained a consistent set of the reaction enthalpies. Experimental results on equilibrium mole fractions and temperature dependencies of equilibrium constants are important for optimization of yields of *tert*-alkyl ethers used as gasoline additives.

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