Chemical equilibrium study in the reacting system of (1-alkoxyethyl)benzene synthesis from isoalkanols and styrene †

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The chemical equilibrium of the reactive systems isoalkanol + styrene \rightleftharpoons (1-alkoxyethyl)benzene (alkyl is isopropyl, *sec*-butyl, and cyclohexyl) was studied in the liquid phase in the temperature range 343 to 433 K using a cation exchanger as heterogeneous catalyst. Enthalpies of reactions, $\Delta_r H_m^\circ$, of (1-alkoxyethyl)benzene synthesis in the liquid phase were obtained from the temperature dependence of equilibrium constants measured in reactive mixtures with an excess of alkanol and showed a good agreement with reaction enthalpies derived from values of the enthalpy of formation $\Delta_r H_m^\circ$ (1) of the participants in the reaction for the synthesis of (1-isopropoxyethyl)benzene, measured by combustion calorimetry. The standard molar enthalpies of vaporization of (1-alkoxyethyl)benzenes were obtained from the temperature dependence of the vapor pressure measured by the transpiration method. Resulting values of $\Delta_r H_m^\circ$ (g) were used to prove the consistency of the experimental data and to derive strain enthalpies of (1-alkoxyethyl)benzenes. The strain effects were discussed in terms of deviations of $\Delta_r H_m^\circ$ (g) from the group additivity rules.

1 Introduction

Enthalpies of *chemical reactions* can be determined experimentally by means of calorimetric measurements (in accordance with the first law of thermodynamics) and from results of studies of chemical equilibrium constants and their temperature dependence (in accordance with the second law of thermodynamics).

The first law method (combustion enthalpy measurement): combustion calorimetry is the conventional method for measuring $\Delta_r H_m^\circ$ of stable species in the condensed state (solid or liquid). Despite the fact that the accuracy of measurements of the energy released in a combustion calorimeter is close to $\pm 0.01\%$, the reliability of the derived enthalpy of combustion is limited by the purity of the sample used. Thus, a lot of reactive, unstable compounds, or even isomers are excluded from thermochemical investigation using this method due to difficulties in their separation, purification or attestation for purity.

The second law method (equilibrium constant measurements): for a chemical reaction in the liquid phase, *e.g.*,

$$\mathbf{A} + \mathbf{B} \rightleftharpoons \mathbf{C} \tag{1}$$

the equilibrium constant, K, is defined as the ratio of the activities a_i of the products and the reagents under equilibrium conditions:

$$K = \frac{a_{\rm C}}{a_{\rm A} a_{\rm B}} \tag{2}$$

From van't Hoff's relation

$$d(\ln K)/dT = \Delta_r H_m^o/RT^2$$
(3)

it is obvious that the slope of a plot $R(\ln K)$ vs. 1/T gives the standard enthalpy of reaction $\Delta_r H^o_m$ if the temperature dependence of the equilibrium constant K is known. From the enthalpy of reaction, $\Delta_r H^o_m$ the enthalpy of formation of one particular species can be determined if those for the other species are known. This procedure, involving study of the changes of equilibrium constants with temperature, is referred to as the *second law method*. Studies of chemical equilibria are essentially less pretentious in comparison to direct calorimetric methods, because mixtures of reactants are usually studied by determining the equilibrium ratios K_x defined as:

$$K_x = \frac{x_{\rm C}}{x_{\rm A} x_{\rm B}} \tag{4}$$

where x_i is the mole fraction of the component *i*. K_x defined by eqn. (4) is related to K in eqn. (2) by

$$K = K_x \frac{\gamma_{\rm C}}{\gamma_{\rm A} \gamma_{\rm B}} \tag{5}$$

where γ_i is the activity coefficient of component *i*. γ_i depends on the composition of the mixture. As a consequence, the measurement of K_x is not sufficient for determining *K*, the knowledge of γ_i of each component at given composition is also required. In some cases, however, the ratio of γ_i -values in eqn. (5) is very close to unity, *e.g.* isomerization equilibria of alkylbenzenes.¹ In this case equilibrium ratios K_x calculated from mole fractions of reaction participants is nearly equal to the true thermodynamic constant *K*. Hence, reaction enthalpy, $\Delta_r H_m^o$, can be calculated from the temperature dependence of the ratio K_x .

The quantitative analysis of the experimental results becomes drastically more complex if one of components of a reacting liquid mixture is *associated* by strong intermolecular forces such as hydrogen bonding. An example is the reacting mixture of methyl *tert*-butyl ether (MTBE) synthesis from

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[†] Electronic supplementary information (ESI) available: experimentally determined compositions of equilibrium mixtures in the reactions of alkanols with styrene; results of combustion experiments. See http://www.rsc.org/suppdata/p2/b2/b200312k/

methanol and isobutene.² In this case the equilibrium ratio K_x [eqn. (4)] depends on the composition of the equilibrium mixture indicating a particularly real (non-ideal) mixture. Taking into account the large scale production of MTBE and similar compounds used as a gasoline additives, elaboration of a general procedure of the thermodynamic interpretation of equilibrium results for associated reacting systems is of increasing importance. In our previous works we developed a procedure to determine K and $\Delta_r H_m^o$ for etherefication reactions³⁻⁵ from experimental data of K_x without measuring activity coefficients γ_i of the reactants. A detailed study of the system α -methylstyrene + methanol \rightleftharpoons methyl cumyl ether \ddagger including phase analysis of the liquid as well as vapor phase has revealed that K_{x} is essentially identical to K in mixture compositions containing an excess of methanol.³ Other systems behave similarly leading to the conclusion that the study of ether synthesis reaction equilibria at compositions with a considerable excess of the alcoholic component allows determination of K without additional measurements of single γ_i -values. The same procedure is applied in this work to further etherification reactions.

Besides widely used methyl *tert*-butyl ether and *tert*-amyl§ methyl ether, (1-alkoxyethyl)benzenes are synthesized in the liquid phase over acid-functionalized ion-exchanged resin catalysts from alkanols and styrene (see Scheme 1). Styrene and



Scheme 1 Reaction of the (1-alkoxyethyl)benzene synthesis (R = methyl, ethyl, isopropyl, propyl, butyl, *sec*-butyl and cyclohexyl).

alkanols are large scale products of the chemical industry and their chemical reactions provide yields of ethers of over 50 mole percent. Therefore (1-alkoxyethyl)benzenes are promising substances for the aforementioned purpose. We have studied systematically the chemical equilibrium in the reacting systems of (1-alkoxyethyl)benzene synthesis such as isopropyl- (iPrEB), sec-butyl- (sBuEB), and cyclohexyl- (c-HexEB) derivatives (see Scheme 1). Values of the reaction enthalpies $\Delta_r H_m^o$ were derived from the temperature dependence of equilibrium ratios K_{y} measured in the reactive mixtures with an excess of alkanol. In order to test the validity of the procedure used, the results obtained have been compared with those calculated from difference of the enthalpies of formation of the reaction participants. For this purpose, standard molar enthalpy of formation in the liquid phase $\Delta_f H_m^o(l)$ of (1-isopropoxyethyl)benzene was additionally obtained from the calorimetrically measured enthalpy of combustion. Further support of the reliability of the procedures applied in this work is expected from the quantitative analysis of standard molar enthalpies of formation in the gaseous phase $\Delta_f H^o_m(g)$. Values of $\Delta_f H^o_m(g)$ of (1-alkoxyethyl)benzenes were obtained from measured values of $\Delta_{f}H_{m}^{o}(l)$ and their enthalpies of vaporization measured by a transpiration method.⁶ Thus, the systematic investigation of the (1-alkoxyethyl)benzene synthesis reactions would be of value for two reasons. First, if good agreement between the standard reaction enthalpies $\Delta_r H_m^o(l)$, obtained from the temperature dependence of the equilibrium constants and those obtained from combustion calorimetry, is found, it would confirm a satisfactory reliability and consistency of our procedure. Second, experimental values of $\Delta_f H_m^o(g)$ would provide useful information on the strain effects and the relation between structure and properties of (1-alkoxyethyl)benzenes. The results of the study can also contribute to an improvement of the Benson⁷ group-contribution methodology.

2 Experimental

2.1 Materials

Styrene, isopropyl alcohol (iPrOH), *sec*-butyl alcohol (*sec*-BuOH), and cyclohexanol (c-HexOH) (water content less than 0.01%) were purchased from Merck. GC analyses gave a purity >99.9% in agreement with specifications. (1-Alkoxyethyl)benzenes were synthesized *via* alkylation of an appropriate alkanol with styrene (see Scheme 1) in the presence of a catalytic amount of cation exchange resin in the H⁺ form (Amberlyst 15, Aldrich) at 343 K. Prior to the experiments the cation exchange resin Amberlyst 15 in H⁺ form was dried for eight hours at 383 K in a vacuum oven at reduced pressure.

Pure samples of (1-alkoxyethyl)benzenes were obtained by repeated distillations at reduced pressure under N_2 , after being dried with molecular sieves (0.4 nm). No impurities could be detected in the samples by GC.

2.2 Chemical equilibrium study

Glass vials with screw caps were filled two-thirds full with the initial liquid mixture of alkanol and styrene. Cation-exchange resin Amberlyst 15 (Aldrich) in the H⁺ form was added as a solid catalyst. The quantity of catalyst was approximately 10% from the weight of the mixture. The vial was thermostatted at temperature $T_i \pm 0.1$ K and periodically shaken. After definite time intervals the vial was cooled rapidly in ice and opened. A sample for GC analysis was taken from the liquid phase using a syringe. The vial was then kept at the same temperature. Samples were withdrawn until no further change of the composition was observed, indicating that the chemical equilibrium was established.

The composition of the reaction mixtures was analysed using a Hewlett Packard gas chromatograph 5890 Series II equipped with a flame ionisation detector and Hewlett Packard 3390A integrator. The carrier gas (nitrogen) flow was 12.1 cm³ s⁻¹. A capillary column HP-5 (stationary phase crosslinked 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 μ m. The standard temperature program of the GC was T = 353 K for 180 s followed by a heating rate of 0.167 K s⁻¹ to T = 523 K. Response factors of all reagents were determined using calibration mixtures of the corresponding components prepared gravimetrically.

2.3 Combustion calorimetry

An isoperibolic calorimeter³ equipped with a static bomb and an isothermal water jacket was used for measuring the energy of combustion of (1-isopropoxyethyl)benzene. The temperature of the water jacket was maintained to within ±0.0015 K using a high precision mercury contact thermometer. To exclude traces of water in the liquid samples used for the combustion experiments, the purified samples were dried over molecular sieves and distilled once more prior to combustion. Each sample was sealed in a container to avoid oxidation and contamination with moisture. In the present study, we used commercially available polythene ampoules (Fa. NeoLab, Heidelberg) of 1 cm³ volume as the sample container for the liquids. The initial temperature of the combustion experiments was 298.15 K for each experiment. The energy equivalent of the calorimeter ε_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39i, N.I.S.T.). From seven experiments, ε_{calor} was determined to be 15296.0 ± 2.3 J K⁻¹. For converting the energy of the actual combustion process to that of the isothermal process, and reducing to standard states, the conventional procedure⁸ was applied. The sample mass of (1-isopropoxyethyl)benzene was reduced to vacuum, taking into consideration the density value $\rho_{(293)} = 0.915 \text{ g cm}^{-3}$ which was determined in a calibrated 10 cm³ pycnometer. The energy

 $[\]ddagger$ The IUPAC name for cumyl is α, α -dimethylbenzyl.

[§] The IUPAC name for tert-amyl is tert-pentyl.

Table 1 Thermochemical data for (1-alkoxyethyl)benzenes at T = 298.15 K ($p^{\circ} = 0.1$ MPa)

	$\Delta_{\rm f} H_{\rm m}^{\rm o}({\rm l})/{\rm kJ}~{\rm mol}^{-1}$	$\Delta_1^{\rm g} H_{\rm m}^{\rm o}/{\rm kJ}~{ m mol}^{-1}$	$\Delta_{\rm f} H_{ m m}^{ m o}({ m g})^{b}/{ m kJ}~{ m mol}^{-1}$	$\Delta_{\rm f} H^{\rm o}_{\rm m}({\rm g})({\rm calc.})^{c}/{\rm kJ}~{\rm mol}^{-1}$	$H_{\rm S}^{d}/{\rm kJ}~{\rm mol}^{-1}$
(1-Isopropoxyethyl)benzene	-233.3 ± 1.0	55.41 ± 0.27	-177.9 ± 1.0	-184.5	6.6
S^*, R^* -(1-sec-Butoxyethyl)benzene	-259.8 ± 2.9^{a}	58.70 ± 0.46	-201.1 ± 2.9	-206.0	4.9
<i>S</i> *, <i>S</i> *-(1- <i>sec</i> -Butoxyethyl)benzene	-258.1 ± 2.9^{a}	59.13 ± 0.48	-199.0 ± 2.9	-206.0	7.0
(1-Cyclohexyloxyethyl)benzene	-263.8 ± 2.2^{a}	69.75 ± 0.45	-194.1 ± 2.3	-207.8	13.7
"Coloulated from the results of the	abamical aquilibrium	study (see tart) b	$\mathbf{A} \mathbf{H}^{0}(\mathbf{a}) = \mathbf{A} \mathbf{H}^{0}(1) + \mathbf{A}^{0}(1)$	U^{0} "Coloulated on the sum	a of stania fac

^{*a*} Calculated from the results of the chemical equilibrium study (see text). ^{*b*} $\Delta_{f}H_{m}^{o}(g) = \Delta_{f}H_{m}^{o}(1) + \Delta_{1}^{g}H_{m}^{o}$. ^{*c*} Calculated as the sum of strain-free increments (see text). ^{*d*} Strain enthalpy of ethylbenzene derivatives $H_{s} = \Delta_{f}H_{m}^{o}(g)(\exp) - \Delta_{f}H_{m}^{o}(g)(\operatorname{calc.})$.

of combustion of the cotton thread $\Delta_c u^o(CH_{1.774}O_{0.887}) = -(16945.2 \pm 4.2) \text{ Jg}^{-1}$ and polythene $\Delta_c u^o(CH_{1.930}) = -46361.0 \pm 3.1 \text{ Jg}^{-1}$ were measured in our laboratory previously.

2.4 Transpiration method

The molar enthalpies of vaporization of the (1-alkoxyethyl)benzenes were determined using the method of transpiration in a saturated N₂-stream and applying the Clausius–Clapeyron equation to vapor pressures measured as function of the temperature. The method has been described before⁶ and has given results in excellent agreement with other established techniques for determining vapor pressures of pure substances in the range of 0.005 to *ca.* 10000 Pa and enthalpies of vaporization, $\Delta_{\rm s}^{\rm g} H_{\rm m}^{\rm o}$, from the temperature dependence of the vapor pressure. Values of $\Delta_{\rm s}^{\rm g} H_{\rm m}^{\rm o}$ at T = 298.15 K are listed in Table 1.

3 Results

3.1 Equilibrium constants and reaction enthalpies

The chemical equilibrium of the reactive systems isoalkanol + styrene \rightleftharpoons (1-alkoxyethyl)benzene was studied in the liquid phase in the temperature range 343 to 433 K. In spite of the fact that equilibrium studies have been performed at elevated temperatures, any corrections of the reaction enthalpies are negligible,³⁻⁵ taking into account the individual error bars of about 1.5 to 3 kJ mol⁻¹ typical of the equilibrium measurements. In further calculations it was assumed that the enthalpy of reaction hardly changes on passing from the average temperature of the experimental range to T = 298.15 K.

3.1.1 The (1-isopropoxyethyl)benzene synthesis reaction. The linear alkanols such as ethanol, propanol, and butanol react rapidly with the styrene without side reactions.⁵ In contrast, reaction of styrene with the branched alkanols is accompanied by a few side reactions. Reactions presented in Scheme 2



Scheme 2 Scheme of (1-isopropoxyethyl)benzene synthesis.

have been observed in the system of (1-isopropoxyethyl)benzene synthesis. The rate of the goal chemical reaction of styrene with the branched alkanol is substantially less then the rate with the linear ones. Together with the goal reaction (1.1), in the presence of the acidic catalyst, dehydration of isopropyl alcohol occurs (1.2). The product of this reaction is propene (C_3H_6). It reacts with the isopropyl alcohol and gives the product diisopropyl ether (reaction 1.3). The dehydration of isopropyl alcohol is irreversible, but the rate of the reversible reaction 1.1 is rapid enough to reach chemical equilibrium of this reaction even along with the slow decomposition of isopropyl alcohol. In contrast to reaction 1.1, reaction 1.3 is very slow and the equilibrium of this reaction was generally not reached during the time necessary for investigation of the goal reaction 1.1.

3.1.2 The (1-isobutoxyethyl)benzene synthesis reaction. Reactions observed in the system of (1-isobutoxyethyl)benzene synthesis are presented in Scheme 3. The rate of the goal chem-



Scheme 3 Scheme of (1-sec-butoxyethyl)benzene synthesis.

ical reaction 2.1 of styrene with the sec-butyl alcohol is again substantially less than with the n-butanol. The goal reaction (2.1), produces two isomers $S^*, R^*-(1-sec-butoxyethyl)$ benzene and S*,S*-(1-sec-butoxyethyl)benzene, which are able to undergo the mutual isomerisation (reaction 2.4) under the given reaction conditions. In presence of the acidic catalyst, dehydration of the sec-butyl alcohol (2.2) produces the isomeric butenes (C_4H_8). These products can react with the sec-butyl alcohol leading to di-sec-butyl ether (reaction 2.3). The dehydration of sec-butyl alcohol is irreversible, but the rate of the reversible reaction 2.1 is rapid, and equilibrium of this reaction could be reached in spite of the slow decomposition of secbutyl alcohol. In contrast, equilibration of the reaction 2.3 is very slow and the equilibrium of this reaction was generally not reached during the time necessary for investigation of the goal to reaction 2.1.

3.1.3 The (1-cyclohexyloxyethyl)benzene synthesis reaction. Reactions observed in the system of (1-cyclohexyloxyethyl)benzene synthesis are presented in Scheme 4. The goal reaction 3.1 is also accompanied by a slow dehydration of cyclohexanol. However, possibly due to high strain, the product of the reaction of cyclohexanol with cyclohexene, dicyclohexyl ether, was not found in the reaction products.



Experimentally determined compositions of equilibrium mixtures (including mole fractions of by-products) and K_{y} values in the liquid phase, obtained from the results of the chemical equilibrium study of the (1-alkoxyethyl)benzene synthesis using eqn. (4) are listed in tables deposited as electronic supplementary information and are presented graphically in Fig. 1. Inspection of these tables and Fig. 1 shows that



Fig. 1 Equilibrium ratios K_x for (1-alkoxyethyl)benzene synthesis as a function of alkanol mole fraction x in the equilibrium mixture at T = 353.1 K.

 K_x -values are almost independent of the mole fraction of alkanol if $x_{AlkOH} > 0.3$. It can be also assumed that the presence of the side reaction products has no significant influence on the on the equilibration of the goal reactions. For all three systems studied, a plot of $\lg K_x$ as a function of 1000/T with K_x -values obtained from the glass vials technique at values of $x_{AlkOH} \ge 0.3$ give straight lines which are almost parallel to each other (see Fig. 2). For comparison other reactions of (1-alkoxyethyl)-



Fig. 2 Equilibrium ratios K_x for (1-alkoxyethyl)benzene synthesis at a mole fraction $x_{alkanol} > 0.3$ as a function of temperature.

benzene synthesis obtained previously are also presented in Fig. 2. Experimental values of K_x have been approximated as a function of temperature by the linear equation $\lg K_x = a +$ $b(1000T/K)^{-1}$ using the method of least squares. The slopes of these lines when multiplied by the gas constant give the standard enthalpy of reaction $\Delta_r H_m^o = -b \times 2.303R$ of the (1-alkoxyethyl)benzene synthesis reaction in the liquid state in kJ mol⁻¹ and the intercept gives the standard entropy of reaction $\Delta_r S_m^\circ = a \times 2.303 R$ in J K⁻¹ mol⁻¹. Numerical results are presented in Table 2.

3.2 Energy of combustion and enthalpy of formation

The results for a typical combustion experiment of (1-isopropoxyethyl)benzene are given in a table deposited as electronic supplementary information. Standard molar enthalpies of combustion $\Delta_{c}H_{m}^{o}(1)$ and of formation $\Delta_{f}H_{m}^{o}(1)$ (see Table 1) were calculated according to the established procedure.⁸ The assigned standard deviation of the mean value of $\Delta_{\rm f} H^{\rm o}_{\rm m}(1)$ includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H₂O and CO₂.

4 Discussion

3.2

3.3

Comparison of the reaction enthalpies obtained from 4.1 equilibrium studies and from combustion experiments

Standard enthalpies of the synthesis reactions of (1-alkoxyethyl)benzenes from isoalkanols and styrene have been obtained in the liquid phase. The validity of these results obtained from the chemical equilibrium study can be verified by comparison with the values of the reaction enthalpies calculated from the formation enthalpies of the reaction participants. For this purpose the standard molar enthalpy of formation $\Delta_{\rm f} H^{\rm o}_{\rm m}(l)$ of (1-isopropoxyethyl)bezene at 298.15 K was measured by means of combustion calorimetry in this work (Table 1). Further experimental data necessary for comparison are available in the literature: for styrene⁹ $\Delta_f H_m^o(l) = (103.4 \pm 100)$ 0.9) kJ mol⁻¹, for isopropyl alcohol ${}^{10}\Delta_{\rm f}H^{\circ}_{\rm m}(l) - (317.0 \pm 0.3)$ kJ mol⁻¹, and for sec-butyl alcohol¹⁰ $\Delta_t H_m^{\circ}(l) = -(342.7 \pm 0.6)$ kJ mol⁻¹. Data for cyclohexanol $\Delta_f H_m^o(l) = -(348.8 \pm 0.2) \text{ kJ mol}^{-1}$ were calculated from its gaseous enthalpy of formation¹¹ $\Delta_{\rm f} H^{\circ}_{\rm m}({\rm g}) = -(286.8 \pm 0.2) \text{ kJ mol}^{-1}$ and enthalpy of vapor-ization¹² $\Delta_{\rm I}^{\rm g} H^{\circ}_{\rm m} = 62.01 \text{ kJ mol}^{-1}$ These data were used to calculate independently $\Delta_{f} H_{m (first law)}^{o}$ of the (1-isopropoxyethyl)benzene (iPrEB) synthesis reaction in the liquid phase:

$$\Delta_{\mathbf{r}} H^{\circ}_{\mathbf{m}}(\mathbf{l})_{(\mathbf{first law})} = \Delta_{\mathbf{f}} H^{\circ}_{\mathbf{m}}(\mathbf{l})_{(\mathbf{iPrEB})} - \Delta_{\mathbf{f}} H^{\circ}_{\mathbf{m}}(\mathbf{l})_{(\mathbf{iPrOH})} - \Delta_{\mathbf{f}} H^{\circ}_{\mathbf{m}}(\mathbf{l})_{(\mathbf{Styrene})} = -(20.0 \pm 3.0) \text{ kJ mol}^{-1} \quad (6)$$

The comparison with experimental values obtained from the chemical equilibrium study is given in Table 2. The calculated values of $\Delta_r H_m^o(l)_{(first law)}$ for the reaction of (1-isopropoxyethyl)benzene is in agreement with those of $\Delta_r H_m^o(l)_{(second law)}$ within the limits of the experimental uncertainties estimated for both methods.

The thermodynamic consistency observed allows calculation of the enthalpy of formation of other (1-alkoxyethyl)benzenes (see Table 1) from the known enthalpies of formation of alkanols, styrene and standard enthalpies of reaction obtained from the temperature dependence of K_x (see Table 2).

Because of the very slow rate, the chemical equilibration of the side reactions of formation of diisopropyl ether (1.3) in Scheme 2 and di-sec-butyl ether (2.3) in Scheme 3 was reached only at certain compositions of the reaction mixture. Equilibrium ratios K_x of these reactions were derived at each temperature of investigation, but the results for of these ratios are less reliable in comparison with those of the goal reactions 1.1

Table 2 Thermodynamic functions $\Delta_r H_m^\circ$ and $\Delta_s S_m^\circ$ of the (1-alkoxyethyl)benzene synthesis reactions in the liquid phase at T = 298.15 K obtained from lg $K_x = a + b(1000 T/K)^{-1}$ and data of $\Delta_r H_m^\circ$ obtained from enthalpies of formation of the reaction participants

Alkyl	$\Delta_{\mathbf{r}} H_{\mathrm{m (second law)}}^{\mathrm{o}} {}^{a}/\mathrm{kJ mol^{-1}}$	$\Delta_r H_{\!m({\rm firstlaw})}^{~~o} ~{}^b/kJ ~mol^{-1}$	а	b	$\langle T \rangle^{c} / \mathbf{K}$	$\Delta_{\rm r} S_{\rm m}^{ m o} {}^{\prime}/{ m J} { m K}^{-1} { m mol}^{-1}$
Iso-Pr	-20.9 ± 0.5	-20.0 ± 3.0	-2.57 ± 0.06	1.09 ± 0.02	383.1	-49.2 ± 1.2
sec-Bu	-20.5 ± 2.7		-2.69 ± 0.36	1.07 ± 0.14	393.1	-51.5 ± 7.0
Cyclo-Hex	-18.4 ± 2.0		-2.03 ± 0.27	0.97 ± 0.10	383.1	-38.9 ± 5.2

^{*a*} Derived from the temperature dependence of K_x . ^{*b*} Calculated from the enthalpies of formation of the reaction participants. ^{*c*} The average temperature of the equilibrium study.

(Scheme 2) and 2.1 (Scheme 3). Experimental values of K_x were approximated as a function of temperature by the linear equation $\lg K_x = -(4.34 \pm 0.36) + (1.95 \pm 0.14)(1000T/K)^{-1}$ for reaction 1.3 (Scheme 2) and $\lg K_x = -(4.21 \pm 0.34) + (1.45 \pm 0.13)(1000T/K)^{-1}$ for reaction 2.3 (Scheme 3) and presented in Fig. 3. The validity of these results obtained from the chemical equilibrium study can be verified by comparison with the values



Fig. 3 Equilibrium ratios K_x for diisopropyl ether and di-*sec*-butyl ether synthesis reactions as a function of temperature.

of the reaction enthalpies calculated from the formation enthalpies of the reaction participants. For this purpose the standard molar enthalpies of formation $\Delta_r H_m^{\circ}(l)$ of appropriate olefins and ethers were taken from the literature.¹³ The calculated values of $\Delta_r H_m^{\circ}(l) = -38.9 \text{ kJ mol}^{-1}$ for the reaction 1.3 (Scheme 3) and $\Delta_r H_m^{\circ}(l) = -28.4 \text{ kJ mol}^{-1}$ for reaction 2.3 (Scheme 3) are in very close agreement being within the limits of experimental uncertainty with those of $\Delta_r H_m^{\circ}(l) = -(37.3 \pm 2.6) \text{ kJ mol}^{-1}$ and $\Delta_r H_m^{\circ}(l) = -(27.8 \pm 2.5) \text{ kJ mol}^{-1}$ derived from the chemical equilibrium study.

Experimental values of K_x of the isomerisation reaction 2.4 of two isomers S^*, R^* -(1-sec-butoxyethyl)benzene and S^*, S^* -(1-sec-butoxyethyl)benzene were approximated as a function of temperature by the linear equation $\lg K_x = -(0.20 \pm 0.032) + (0.088 \pm 0.013)(1000T/K)^{-1}$. The enthalpy of this reaction $\Delta_r H^o_m(l) = -(1.68 \pm 0.24)$ kJ mol⁻¹ was derived from the chemical equilibrium study and used to obtain enthalpies of formation $\Delta_r H^o_m(l)$ of both isomers with help of the reaction 2.1 and enthalpies of formation of its participants (see Table 1).

4.2 Strain enthalpies $H_{\rm S}$ of (1-alkoxyethyl)benzenes

An important test to establish the validity of the experimental and calculation procedures presented in this paper provides the comparison of strain enthalpies of (1-alkoxyethyl)benzenes, which were derived from their gaseous standard molar enthalpies of formation $\Delta_{\rm f} H_{\rm m}^{\circ}({\rm g})$ at 298.15 K. Indeed, the isopropoxy, *sec*-butoxy, and cyclohexyloxyethylbenzenes listed in Table 1 present a typical example of the homologous series. It is well established that for such series^{4,5} the enthalpic contribution into $\Delta_{\rm f} H_{\rm m}^{\circ}({\rm g})$ from the CH₂-group should remain constant. In other words, no additional strain interactions in a molecule are expected by passing from methoxy to butoxyethylbenzene. The resulting values of $\Delta_r H^o_m(g)$ of (1-alkoxyethyl)benzenes calculated as sum of $\Delta_r H^o_m(l)$ and $\Delta_l^g H^o_m$ are shown in Table 1.

We define the strain enthalpy $H_{\rm s}$ of a molecule as the difference between the experimental standard enthalpy of formation $\Delta_{\rm f} H^{\rm o}_{\rm m}({\rm g})$ and the calculated sum of the strain-free Benson type increments⁷ for this molecule. The strain-free increments for the calculation of enthalpies of formation of alkanes,¹⁴ alkylbenzenes¹⁵ and ethers^{16,17} are already well established. By using these group-additivity parameters and the values of $\Delta_{\rm f} H^{\rm o}_{\rm m}({\rm g})$ of ethylbenzene derivatives (Table 1) and their values of strain enthalpies $H_{\rm s} = [\Delta_{\rm f} H^{\rm o}_{\rm m}({\rm g}) - \Sigma$ increments] have been estimated (Table 1).

(1-Isopropoxyethyl)benzene and (1-isobutoxyethyl)benzene studied here are very similarly strained by about 5 kJ mol⁻¹ (Table 1). This fact is a further indication that the data for $\Delta_{\rm f} H_{\rm m}^{\rm o}({\rm g})$ of (1-alkoxyethyl)benzenes, obtained by combining the different experimental techniques (calorimetry, transpiration, equilibrium study) generally consistently support confidence in the experimental procedures used. What causes strain in these molecules? Elucidation of the nature of strain in (1alkoxyethyl)benzene is aided by comparison with the strain of similarly shaped isopropylbenzene:¹³ $\Delta_f H_m^o(g) = -(3.9 \pm 1.1) \text{ kJ}$ mol^{-1} and strain enthalpy $H_s = 5.0 \text{ kJ mol}^{-1}$. Isopropylbenzene is a relevant structural pattern of strain in the (1-alkoxyethyl)benzenes studied. Its strain enthalpy is a reflection of the intrinsic strain of the molecule due to steric repulsions of methyl groups and the benzene ring attached to the central tertiary carbon atom. It is expected from the analogy with the strain of isopropylbenzene, that the observed amount of destabilization in alkoxyethylbenzene derivatives could most likely be attributed to the steric repulsions of methyl groups and the benzene ring attached to the central tertiary carbon atom. Therefore it can be concluded that no additional groupadditivity parameters or correction terms are necessary (besides the correction for $H_{\rm S} = 5.0 \text{ kJ mol}^{-1}$ like in isopropylbenzene) for the group-contribution correlation for $\Delta_{\rm f} H^{\rm o}_{\rm m}({\rm g})$ of the similarly shaped (1-alkoxyethyl)benzenes. It is obvious, that the somewhat larger strain of the (1-cyclohexyloxyethyl)benzene $(H_{\rm s} = 13.7 \text{ kJ mol}^{-1}$, see Table 1) is caused by an additional contribution from the strain of the cyclohexyl substituent attached to the oxygen atom. For comparison, the strain of the cyclohexanol itself is ¹³ $H_s = 8.8 \text{ kJ mol}^{-1}$.

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