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Study of the Chemical Equilibrium of the Liquid-Phase Dehydration of 1-Hexanol to Dihexyl Ether

Roger Bringué, Javier Tejero,* Montserrat Iborra, Carles Fité, José Felipe Izquierdo, and Fidel Cunill

Chemical Engineering Department, University of Barcelona. C/Martí i Franquès 1, 08028 Barcelona, Spain

The equilibrium constants of the liquid-phase dehydration of 1-hexanol to dihexyl ether (DNHE) and water were determined in the temperature range of (423 to 463) K on Amberlyst 70. The equilibrium constants of the two main side reactions, DNHE decomposition to 1-hexene and 1-hexanol and isomerization of 1-hexene to 2-hexene, were also studied. The etherification reaction proved to be slightly exothermic, with an enthalpy change of reaction of $-(9.5 \pm 0.2)\ \mathrm{kJ \cdot mol^{-1}}$ at 298 K. From this value, the standard formation enthalpy and molar entropy of DNHE were computed to be $-(478.6 \pm 0.8)\ \mathrm{kJ \cdot mol^{-1}}$ and $(517.4 \pm 0.5)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively. A correction concerning the effect of pressure on the entropy proved to be necessary when computing liquid-phase entropy from gas-phase data. The isomerization of 1-hexene to 2-hexene is exothermic, whereas the decomposition of DNHE is endothermic.

Introduction

In contrast with the U.S. market,[1] which is clearly gasoline dominated, the European consumption of diesel fuel is much higher than that of gasoline, and it is increasing year by year.[2] This fact, together with the increasingly stringent specifications from legislation to improve air quality, leads to a fuel revolution: more diesel fuel and higher quality is necessary.

Forthcoming diesel fuels will likely be characterized by a higher cetane number, lower density, and lower aromatics, polyaromatics, and sulfur contents with respect to the current diesel fuels. A feasible option for complying with these regulations might be the use of reformulated diesel fuels that contain appropriate high-quality components,[3] for example, oxygenates, because classical diesel additives are too expensive to be used in large amounts. Previous studies concluded that linear ethers with at least nine carbon atoms present high cetane numbers and desirable cold flow properties.[4] In Table 1, the main characteristics of some linear ethers as fuel components are shown,[5] and they are compared with standard diesel fuel specifications. The cetane number of the proposed ethers is twice that of commercial diesel, and cold flow properties are considerably improved. Density and viscosity are also more favorable.

Among the ethers in Table 1, dipentyl ether (DNPE) and dihexyl ether (DNHE) constitute feasible options because they can be produced from the alcohols 1-pentanol and 1-hexanol, which are obtained from hydroformylation and hydrogenation of C_4 and C_5 linear olefins, respectively. The production of high cetane ethers from linear olefins is promising because it allows us to substitute the olefins, which are undesirable because of their high ozone formation potential.

Table 1. Properties of Some Linear Ethers: Density, ρ; Boiling Point, T_b; Viscosity, ν; Cloud Point, CP; Cold Filter Plugging Point, CFPP; Flash Point, FP

	diesel	DNPE[a]	DNHE[b]	MOE[c]	DNPM[d]
ρ (279 to 293) K/kg·m^{-3}	850	787	793	790	840
T_b/K	443 to 653	460	502	N/A[e]	491
ν/cSt	3 to 4	1.6	N/A	0.9	N/A
cetane no.	48 to 51	109	118	89	97
CP/K[f]	271 to 278	253	268	256	273
CFPP/K[f]	269 to 276	251	266	N/A	266
FP/K[f]	340	330	351	N/A	N/A

[a] Dipentyl ether. [b] Dihexyl ether. [c] Methyl-octyl ether. [d] Dipentoxy methane. [e] N/A: not available. [f] Blending properties.

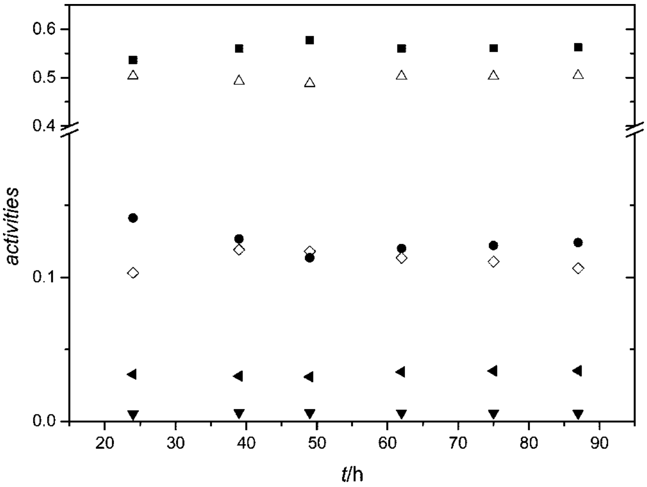

Figure 1. Evolution of activities during an experiment at 463 K over time. Tilted solid triangle, hexanol; ●, DNHE; ■, water; ▼, 1-hexene; ◇, 2-hexene; Δ, dioxane.

The description,[6] kinetics,[7] and thermodynamics[8] of the 1-pentanol dehydration reaction were studied in former works. DNHE synthesis has not yet been studied in detail. In liquid phase, the dehydration of 1-hexanol to DNHE and water is reported on only Nafion NR50 at 423 K.[9] To the best of our knowledge, thermodynamic data of this reaction, such as the enthalpy change of reaction and equilibrium constants, have not been reported. The aim of this work is to determine experimental values of the equilibrium constant of the dehydration of 1-hexanol to DNHE and water by direct measurement of the mixture composition at equilibrium. From these values, thermodynamic data are computed and compared with estimated and experimental values found in data banks. The decomposition

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* Corresponding author. E-mail: jtejero@ub.edu.

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Table 2. Experimental Conditions and Calculated Equilibrium Constants for the Dehydration of 1-Hexanol to DNHE and Water (DNHE Superscript), DNHE Decomposition to 1-Hexanol and 1-Hexene (1-Hexene Superscript), and Isomerization of 1-Hexene to *cis*- and *trans*-2-Hexene (2-Hexene Superscript)

T/K	K_x^{DNHE}	K_γ^{DNHE}	K_a^{DNHE}	$K_x^{\text{1-hexene}} \cdot 10^4$	$K_\gamma^{\text{1-hexene}}$	$K_a^{\text{1-hexene}} \cdot 10^4$	$K_x^{\text{2-hexene}}$	$K_\gamma^{\text{2-hexene}}$	$K_a^{\text{2-hexene}}$
423	21.0	3.04	69.5 ± 0.6	1.9	1.00	1.9 ± 0.1	23.1	1.07	24.7 ± 0.3
433	20.3	3.06	65.7 ± 2.1	3.2	1.00	3.2 ± 0.2	21.2	1.07	22.6 ± 0.8
443	19.3	3.22	62.0 ± 0.9	8.8	1.05	9.3 ± 0.3	21.4	1.05	22.5 ± 0.3
453	19.5	3.24	59.5 ± 0.4	7.5	1.01	7.6 ± 0.2	19.0	1.06	20.1 ± 0.2
463	18.5	3.31	56.3 ± 0.5	15.2	1.07	16.3 ± 0.5	18.6	1.04	19.3 ± 0.3

Table 3. Molar Volumes of 1-Hexanol, DNHE, Water, 1-Hexene and 2-Hexene, and K_Γ Correction Factors for the Three Reactions[a]

$\frac{T}{\text{K}}$	$\frac{V_{\text{HeOH}}}{\text{L} \cdot \text{mol}^{-1}}$	$\frac{V_{\text{DNHE}}}{\text{L} \cdot \text{mol}^{-1}}$	$\frac{V_{\text{water}}}{\text{L} \cdot \text{mol}^{-1}}$	$\frac{V_{\text{1-hexene}}}{\text{L} \cdot \text{mol}^{-1}}$	$\frac{V_{\text{2-hexene}}}{\text{L} \cdot \text{mol}^{-1}}$	K_Γ^{DNHE}	$K_\Gamma^{\text{1-hexene}}$	$K_\Gamma^{\text{2-hexene}}$
423	0.145	0.235	0.019	0.178	0.156	0.98	1.05	0.99
433	0.147	0.238	0.019	0.182	0.160	0.98	1.05	0.99
443	0.149	0.241	0.020	0.188	0.164	0.98	1.05	0.99
453	0.152	0.244	0.020	0.195	0.169	0.98	1.05	0.99
463	0.154	0.248	0.020	0.203	0.176	0.98	1.06	0.99

[a] Calculated by the HBT method.[14]

of DNHE to 1-hexanol and 1-hexene and its isomerization to 2-hexene under equilibrium conditions are also studied. Finally, the effect of pressure on the entropy when gas-phase data are converted to liquid-phase data is discussed.

Experimental Section

Chemicals. 1-Hexanol (99.5 % pure, < 0.3 % 2-methyl-1-pentanol, 0.1 % water) was used after purification in a distillation column of the alcohol supplied by Fluka (≥ 98 %). Dihexyl ether was obtained in our laboratory from 1-hexanol dehydration and was purified by distillation to ≥ 98 %. 1-Hexene (≥ 99 %) was supplied by Aldrich, and *trans*-2-hexene (≥ 98 %), *cis*-2-hexene (≥ 95 %), *trans*-3-hexene (≥ 97 %), *cis*-3-hexene (≥ 95 %), and 2-methyl-1-pentanol (≥ 99 %) were supplied by Fluka. 1,4-Dioxane (99.5 %) was supplied by Panreac.

The thermally stable resin Amberlyst 70 (Rohm and Haas) that is used as a catalyst is a macroporous, halogenated, and sulfonated copolymer of styrene/divinylbenzene (S/DVB) in H^+ form with a maximum operating temperature of 473 K. The acidity of the ion-exchange resin was measured by titration against standard base,[10] resulting in 3.01 mequiv H^+ (g of dry resin)$^{-1}$. The catalyst was used in its commercial form (mean bead diameter = 570 μm) after being dried overnight at 373 K under vacuum.

Apparatus. Experiments were carried out in a 100 mL stainless steel autoclave operated in batch mode. A magnetic drive turbine was used for mixing, and baffles were placed inside the reactor to improve the agitation. Temperature was controlled to within ± 1 K by an electric furnace. The pressure was set to 1.6 MPa by means of N_2 to maintain the reacting mixture in the liquid phase over the whole temperature range. One of the reactor outlets was directly connected to a liquid sampling valve, which injected 0.2 μL of pressurized liquid into a gas−liquid chromatograph. More detailed information can be found elsewhere.[7]

Analysis. The composition of liquid mixtures was analyzed by the use of a split mode operation in an HP6890A GLC apparatus (Hewlett-Packard) equipped with a TCD detector. A (50 m)·(0.2 mm)·(0.5 μm) methyl silicone capillary column was used to separate and quantify 1,4-dioxane, 1-hexanol, DNHE, water, C_6 alkenes (1-hexene, 2-hexene, and 3-hexene), and branched ethers (1-(1-methylpentoxy)-hexane, 1-(2-methylpentoxy)-hexane, 2-(1-methylpentoxy)-hexane and 2-(2-methylpentoxy)-hexane). The column was temperature programmed with a 6 min initial hold at 318 K, followed by a 30 K·min^{-1} ramp to 453 K and held for 10 min. Helium was used as carrier gas at a total flow rate of 30 mL·min^{-1}.

Procedure. To ensure that a single phase exists through equilibrium experiments, 1,4-dioxane was used as a solvent. 1,4-Dioxane was selected because it is stable (from physical and chemical standpoints) under working conditions and also because it is easily determined in the chromatographic analysis performed. This methodology was tested by Delion et al.[11] in the liquid-phase hydration of isobutene with eight different solvents. They concluded that the presence of a solvent modifies the equilibrium position of the reaction because the activities of all of the compounds are also modified. However, the equilibrium constants computed from the equilibrium activities of all of the systems were in agreement with the thermodynamic equilibrium constant; that is, the methodology proved to be suitable for measuring such constants.

Catalyst particle diameter measurements were performed in 1,4-dioxane media to check whether it has any influence on the catalyst structure. A Beckman Coulter LS particle size analyzer coupled to a universal liquid module was used for this purpose. Results showed that 1,4-dioxane did not swell the catalyst particles. Blank experiments performed with the same amount of catalyst as that used in subsequent equilibrium experiments showed that 1,4-dioxane did not react under the experimental conditions.

Different mixtures of 1,4-dioxane, 1-hexanol, dihexyl ether, water, and 1-hexene and 2-hexene (*cis* and *trans*) (70 mL) near equilibrium composition were charged into the reactor together with the dried catalyst and, after the system was checked for leakages, heated to the desired temperature. To monitor the concentration variation of chemicals over time, we periodically took liquid samples out of the reactor and analyzed them as mentioned above.

Experiments were performed in the temperature range of (423 to 463) K. The stirring speed was fixed at 350 rpm to prevent catalyst particle attrition. The catalyst load varied from (1 to 4) g, depending on the temperature, to shorten the experiment landing at lower temperatures. Experiments were finished when equilibrium conditions were reached. This was shown in subsequent analysis when the experimental thermodynamic equilibrium constants reached a constant value within the limits of the experimental uncertainties.

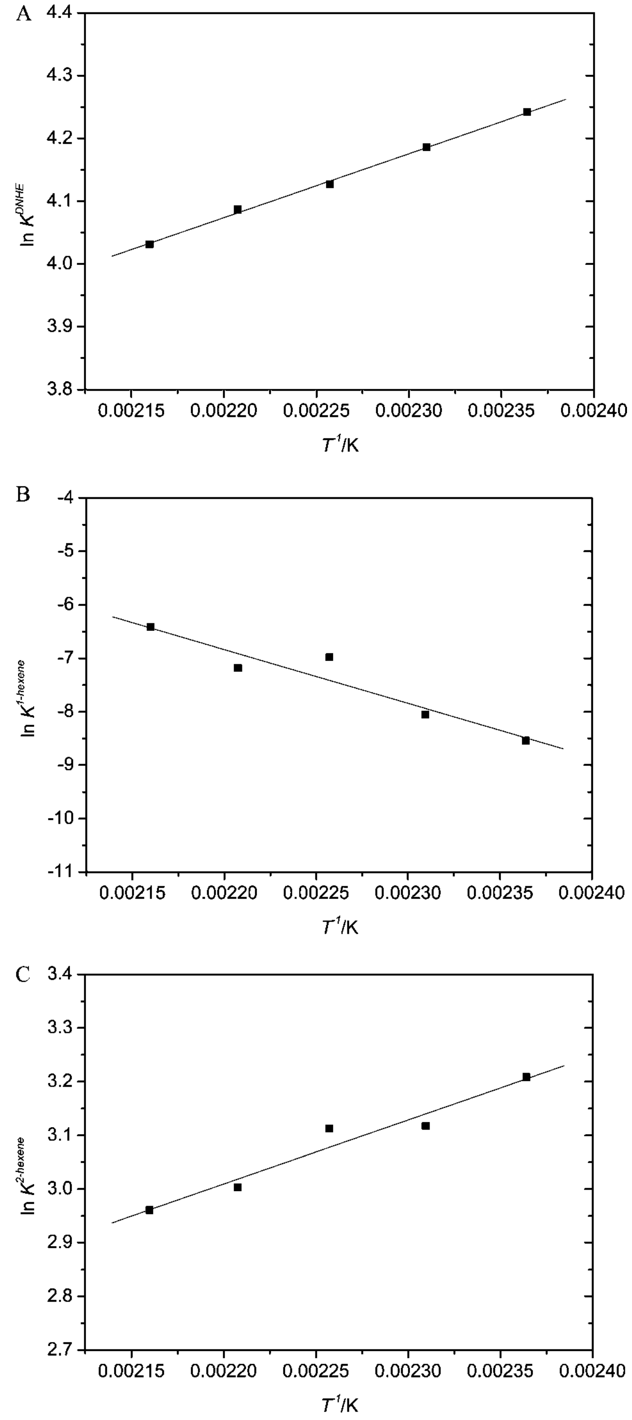
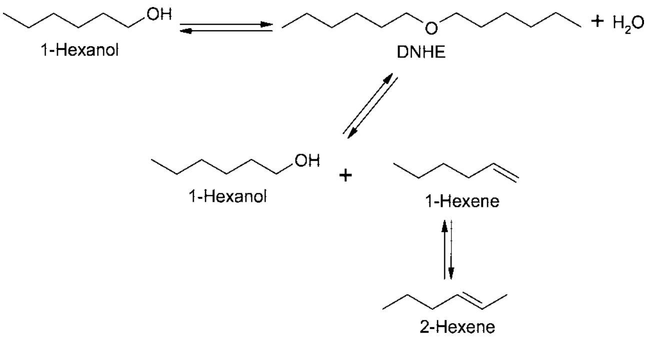


Figure 2. ln *K* versus 1/*T*. Comparison of values obtained experimentally and those predicted from equations 10, 11, and 12 (solid line). (A) DNHE synthesis reaction, (B) DNHE decomposition reaction, and (C) 1-hexene isomerization reaction.

Results

Besides dioxane, 1-hexanol, and the products of the dehydration reaction (DNHE and water), some C_6 alkenes were detected during the equilibrium experiments (mainly 2-hexene but also 1-hexene and 3-hexene). Furthermore, some secondary alcohols, such as 2-hexanol, and branched ethers were detected in very small amounts.

1-Hexene can be formed by monomolecular dehydration of 1-hexanol or by DNHE decomposition. In the latter reaction 1-hexanol is also produced. Because the alcohol concentration was very low throughout the experiments, the most likely reaction that produced 1-hexene is the decomposition of the linear ether, as in the analogous dehydration reaction of 1-pentanol to produce dipentyl ether (DNPE).[8] 2-Hexene was formed by isomerization of 1-hexene. The proposed reaction scheme is the following.



To consider the nonideality of the mixture, we estimated activity coefficients of compounds, γ_i, by the UNIFAC-Dortmund predictive method, [12] and activities, a_i, were then computed. The thermodynamic equilibrium constant for a liquid-phase reaction of a nonideal system is given by

$$K_a = \prod_{i=1}^{S} (a_i')_e^{\nu_i} = \prod_{i=1}^{S} (\gamma_i)_e^{\nu_i}(x_i)_e^{\nu_i} = \prod_{i=1}^{S} (\gamma_i)_e^{\nu_i} \prod_{i=1}^{S} (x_i)_e^{\nu_i} = K_\gamma \cdot K_x \tag{1}$$

K_γ^j was calculated as

$$K_\gamma^{\text{DNHE}} = \frac{\gamma_{\text{DNHE}} \cdot \gamma_{\text{water}}}{\gamma_{\text{1-hexanol}}^2} \tag{2}$$

$$K_\gamma^{\text{1-hexene}} = \frac{\gamma_{\text{1-hexene}} \cdot \gamma_{\text{1-hexanol}}}{\gamma_{\text{DNHE}}} \tag{3}$$

$$K_\gamma^{\text{2-hexene}} = \frac{\gamma_{\text{2-hexene}}}{\gamma_{\text{1-hexene}}} \tag{4}$$

where superscripts DNHE, 1-hexene, and 2-hexene refer to 1-hexanol dehydration to DNHE and water, DNHE decomposition reaction to 1-hexanol and 1-hexene, and 1-hexene isomerization to 2-hexene, respectively. K_x^j was calculated in a similar way by the use of molar fractions instead of activity coefficients

$$K_x^{\text{DNHE}} = \frac{x_{\text{DNHE}} \cdot x_{\text{water}}}{x_{\text{1-hexanol}}^2} \tag{5}$$

$$K_x^{\text{1-hexene}} = \frac{x_{\text{1-hexene}} \cdot x_{\text{1-hexanol}}}{x_{\text{DNHE}}} \tag{6}$$

$$K_x^{\text{2-hexene}} = \frac{x_{\text{2-hexene}}}{x_{\text{1-hexene}}} \tag{7}$$

Figure 1 shows the temporal evolution of activities of 1,4-dioxane, DNHE, 1-hexanol, water, 1-hexene, and 2-hexene during an experiment at 463 K. Activities evolved to reach equilibrium conditions. Dioxane and water were the species with higher activities in the mixture and were very far from the others. High dioxane activity was due to its high concentration (about 50 % mass fraction). High water activity is explained by its high activity coefficient. The activities of 1-hexene were always very small because of its low molar fraction. This fact supposed a drawback for the equilibrium characterization because 1-hexene concentrations were near the detector threshold of the chromatograph, especially at lower temperatures.

Table 2 shows the calculated equilibrium constants for the three chemical reactions. Replicate runs were made at some temperatures, and the reproducibility of experiments was found to be reliable with experimental uncertainties of less than 5 %. Equilibrium constant values presented in Table 2 are the average of those calculated at equilibrium during each experiment. As can be seen, values of K_γ^{DNHE} were significantly different from unity, which shows the nonideality of the mixture because of the presence of water. Furthermore, the large values of K_a^{DNHE} and $K_a^{\text{2-hexene}}$ indicate that the dehydration of 1-hexanol and the isomerization of 1-hexene reactions are mainly shifted to the products. From data of Table 2, it can be concluded that the dehydration of 1-hexanol to DNHE and the isomerization of 1-hexene to 2-hexene are exothermic because their thermodynamic equilibrium constants decrease with temperature. The ether decomposition reaction is endothermic.

Deviation in K_a values due to the difference between the working pressure and the pressure at the standard state was evaluated by means of the Poynting correction factor K_Γ[13]

$$K_\Gamma = \exp\left[\frac{(P/\mathrm{atm}) - 1}{R\cdot(T/\mathrm{K})}\sum_{i=1}^{S}\nu_i\cdot\left(V_i/\mathrm{L}\cdot\mathrm{mol}^{-1}\right)\right] \tag{8}$$

where V_i is the molar volume of compound i.

Molar volumes[14] and K_Γ correction factors for the three reactions are shown in Table 3. It can be seen that by neglecting K_Γ an error in the calculation of K_a is introduced that is lower than the experimental uncertainty. Therefore, it can be assumed that the equilibrium constant depends on only temperature.

The thermodynamic equilibrium constant can be related to thermodynamic variables of the reaction system by

$$\ln K_a = \left(\frac{-\Delta_\mathrm{r}G^0_{(\mathrm{l})}}{RT}\right) = \left(\frac{-\Delta_\mathrm{r}H^0_{(\mathrm{l})}}{RT} + \frac{\Delta_\mathrm{r}S^0_{(\mathrm{l})}}{R}\right) \tag{9}$$

If the enthalpy change of reaction is assumed to be constant over the temperature range, by fitting eq 9 to experimental values of the equilibrium constant at different temperatures (Figure 2), the standard molar enthalpy change of reaction, $\Delta_\mathrm{r}H_{(\mathrm{l})}{}^0$, can be obtained from the slope, and the standard molar entropy change of reaction, $\Delta_\mathrm{r}S_{(\mathrm{l})}{}^0$, can be obtained from the intercept. It can be seen that the fit for the main reaction is very accurate. The other two reactions present some deviations but are globally satisfactory.

The experimental temperature dependence of K_a for each reaction was found to be

$$\ln K_a^{\mathrm{DNHE}} = \frac{(1019.7 \pm 26.5)}{T/\mathrm{K}} + (1.83 \pm 0.06) \tag{10}$$

$$\ln K_a^{\text{1-hexene}} = \frac{(-10067.0 \pm 1877.1)}{T/\mathrm{K}} + (15.3 \pm 4.2) \tag{11}$$

$$\ln K_a^{\text{2-hexene}} = \frac{(1193.5 \pm 158.7)}{T/\mathrm{K}} - (0.38 \pm 0.36) \tag{12}$$

As a consequence, on the assumption that $\Delta_\mathrm{r}H_{(\mathrm{l})}{}^0$and $\Delta_\mathrm{r}S_{(\mathrm{l})}{}^0$ are independent of temperature, the following values are deduced for every reaction

$$\text{DNHE:}\quad \Delta_\mathrm{r}H^0_{(\mathrm{l})} = -(8.5 \pm 0.2)\ \mathrm{kJ\cdot mol^{-1}}$$
$$\Delta_\mathrm{r}S^0_{(\mathrm{l})} = (15.2 \pm 0.5)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$\text{1-Hexene:}\quad \Delta_\mathrm{r}H^0_{(\mathrm{l})} = (84 \pm 16)\ \mathrm{kJ\cdot mol^{-1}}$$
$$\Delta_\mathrm{r}S^0_{(\mathrm{l})} = (121 \pm 82)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$\text{2-Hexene:}\quad \Delta_\mathrm{r}H^0_{(\mathrm{l})} = -(9.9 \pm 1.3)\ \mathrm{kJ\cdot mol^{-1}}$$
$$\Delta_\mathrm{r}S^0_{(\mathrm{l})} = (3 \pm 3)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Considering that the standard enthalpy of reaction significantly changes over the temperature range and a polynomial forms dependence on temperature for molar liquid-phase heat capacities,[13,14] the dependence of $\Delta_\mathrm{r}H_{(\mathrm{l})}{}^0$, $\Delta_\mathrm{r}S_{(\mathrm{l})}{}^0$, the standard free energy change of reaction in liquid-phase, $\Delta_\mathrm{r}G_{(\mathrm{l})}{}^0$, and K_a on temperature can be computed by integrating the Kirchhoff and the van't Hoff equations, as quoted elsewhere[8]

$$\Delta_\mathrm{r}H^0_{(\mathrm{l})} = I_K + aT + \frac{b}{2}T^2 + \frac{c}{3}T^3 + \frac{d}{4}T^4 \tag{13}$$

$$\Delta_\mathrm{r}S^0_{(\mathrm{l})} = R\cdot I_H + a + a\ln T + bT + \frac{c}{2}T^2 + \frac{d}{3}T^3 \tag{14}$$

$$\Delta_\mathrm{r}G^0_{(\mathrm{l})} = I_K - R\cdot I_H T - aT\ln T - \frac{b}{2}T^2 - \frac{c}{6}T^3 - \frac{d}{12}T^4 \tag{15}$$

$$\ln K_a = I_H - \frac{I_K}{RT} + \frac{a}{R}\ln T + \frac{b}{2R}T + \frac{c}{6R}T^2 + \frac{d}{12R}T^3 \tag{16}$$

The integration constants I_K and I_H can be calculated from the temperature dependence relationship for the experimental equilibrium constant of each reaction. By fitting eq 16 to the experimental values of equilibrium constant at different temperatures (Figure 3), I_K can be obtained from the slope and I_H can be obtained from the intercept.

In Table 4, thermochemical data of the compounds involved in the three reactions are shown. Some of the thermochemical data used in this work were estimated because of the lack of experimental data published in the literature (e.g., for DNHE,

Table 4. Thermochemical Data of 1-Hexanol, DNHE, Water, 1-Hexene and 2-Hexene

property	1-hexanol	DNHE	water	1-hexene	2-hexene
$C_{pi} = a_i + b_iT + c_iT^2 + d_iT^3/\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$					
$a_i/\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$	200.805^a	317.828^a	106.61^b	-461.284^a	-268.659^a
$b_i/\mathrm{J\cdot mol^{-1}\cdot K^{-2}}$	0.0701	0.1123	−0.2062	5.3221	3.4110
$c_i/\mathrm{J\cdot mol^{-1}\cdot K^{-3}}$	$2.303\cdot10^{-4}$	$9.9226\cdot10^{-4}$	$3.777\cdot10^{-4}$	−0.0151	−0.00916
$d_i/\mathrm{J\cdot mol^{-1}\cdot K^{-4}}$	$1.56\cdot10^{-7}$	$-6.20\cdot10^{-7}$	$-1.226\cdot10^{-7}$	$1.52\cdot10^{-5}$	$9.17\cdot10^{-6}$
$\Delta_\mathrm{f}H^0{}_{(\mathrm{l})}$ (298.15 K)/kJ·mol^{-1}	$(-377.5 \pm 0.4)^c$	-481.1^d	$(-285.830 \pm 0.040)^e$	$(-72.7 \pm 1.2)^f$	$(-82.6 \pm 0.8)^g$
$S^0{}_\mathrm{g}$ (298.15 K)/J·mol^{-1}·K^{-1}	$(439.7 \pm 2.1)^h$	-418.1^d	$(188.835 \pm 0.010)^e$	387.1^i	383.6^i
$S^0{}_\mathrm{l}$ (298.15 K)/J·mol^{-1}·K^{-1}	287.4^j	517.8^k	$(69.95 \pm 0.03)^e$	295.18^l	285.6^k
$\Delta_\mathrm{vap}H$ (298.15 K)/kJ·mol^{-1}	61.6^m	64.1^m	45.051^n	30.6^o	31.5^o

[a] a_i, b_i, c_i, and d_i estimated by Rowlinson−Bondi method and fit to a third-order equation.[14] [b] Calculated from Shomate equation and fit to a third-order equation.[15] [c] Mosselman et al.[16] [d] Estimated by modified Benson method.[17] [e] Cox et al.[18] [f] Molnar et al.[19] [g] Rogers et al.[20] [h] Green.[21] [i] Estimated by Benson method.[14] [j] Kelley.[22] [k] Calculated from eq 17. [l] McCullough et al.[23] [m] Majer et al.[24] [n] At 273.15 K, Murphy et al.[25] [o] Camin et al.[26]

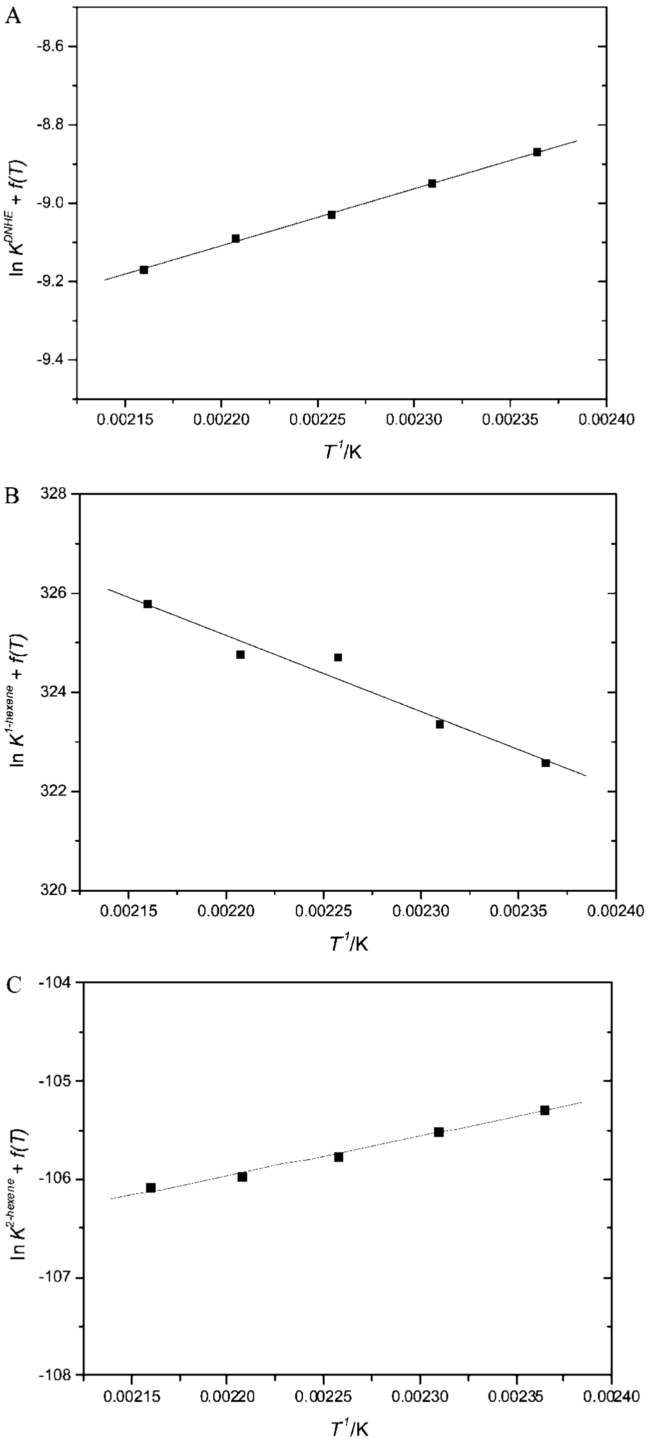


Figure 3. ln $K + f(T)$ versus $1/T$. Comparison of values obtained experimentally and those predicted from equation 16 with data of Table 6 (solid line). (A) DNHE synthesis reaction, (B) DNHE decomposition reaction, and (C) 1-hexene isomerization reaction.

Table 5. Liquid-Phase Entropy Calculated from S^0_g and $\Delta_{vap}H$ (S^0_l*calcd) and Computed Considering the Effect of the Pressure Expressed by Equation *17* (S^0_lcalcd)

	1-hexanol	DNHE	water	1-hexene	2-hexene	DNPE
S^0_lexptl/J·mol^{-1}·K^{-1}	287.4	517.4[a]	69.95	295.18		473.7[b]
S^0_l*calcd/J·mol^{-1}·K^{-1}	233.1	449.5	37.7	284.4	277.9	399.4
% dif.	−19	−13	−46	−4		−16
S^0_lcalcd/J·mol^{-1}·K^{-1}	286.8	517.8	66.6	296.6	285.6	453.8
% dif.	−0.2	0.1	−5	0.5		−4

[a] Proposed in this work. [b] Bringué et al.[7]

Table 6. Temperature Dependence Parameters of *K*, $\Delta H_{(l)}{}^0$, $\Delta S_{(l)}{}^0$, $\Delta G_{(l)}{}^0$ for the Three Chemical Reactions, as Shown in Equations *13*, *14*, *15*, and *16*

	DNHE	1-hexene	2-hexene
I_K/J·mol^{-1}	−11 815.7	127 766.9	−33 319.9
I_H/J·mol^{-1}	−12.233	358.959	−114.779
a/J·mol^{-1}·K^{-1}	22.832	−578.307	192.625
b/J·mol^{-1}·K^{-2}	−0.23403	5.27983	−1.91113
c/J·mol^{-1}·K^{-3}	9.0933·10^{-4}	−1.5862·10^{-2}	5.9436·10^{-3}
d/J·mol^{-1}·K^{-4}	−1.0550·10^{-6}	1.5964·10^{-5}	−6.0138·10^{-6}

only the enthalpy of vaporization, $\Delta_{vap}H$, at 298.15 K was available). Liquid-phase molar heat capacities, $C_{p,l}$, were estimated by means of the Rowlinson−Bondi[14] method from gas-phase molar heat capacities data, $C_{p,g}$, and $C_{p,l}$ values obtained were fit to a third-order polynomial equation. Liquid-phase standard molar enthalpy change of formation, $\Delta_f H^0_{(l)}$, and gas-phase molar entropy, S^0_g, of DNHE were estimated by an improved Benson method proposed by Verevkin[17] that is applicable for alkyl ethers among other oxygenated compounds. S^0_g of the two alkenes was estimated by the standard Benson method.[14] For DNHE and 2-hexene, liquid-phase molar entropy, S^0_l was estimated from gas-phase data and $\Delta_{vap}H$ by the use of the following equations[27,28]

$$S^0_l = S^0_g - \Delta_v S^0 - \Delta_c S^0 - \Delta_{ig} S^0 \tag{17}$$

where

$$\Delta_v S^0 = \frac{\Delta_{vap}H}{T} \tag{18}$$

$$\Delta_c S^0 = -R \ln\left(\frac{P}{P^s}\right) \tag{19}$$

$$\Delta_{ig} S^0 = \frac{27}{32}\frac{RT_c^3}{P_c T^3}P \tag{20}$$

Equation 18 accounts for the entropy change due to phase change, which is the correction usually used to calculate liquid-phase entropy from gas-phase data. However, pressure affects the entropy of a gas and must be taken into consideration in entropy evaluations.[28] To evaluate the effect of pressure variation, Stull et al. proposed the correction factors shown in eqs 19 and 20. First, we consider the effect of the vapor compression from the saturation pressure, P^s (vapor pressure at standard temperature), on the standard pressure (101.325 kPa), which is expressed by eq 19. If the vapor pressure of the compound is low, then the correction proposed by eq 19 is quite important; therefore, the value of S^0_l would be underestimated if not considered. Second, we consider the entropy increment between an ideal gas under standard conditions ($P = 101.325$ kPa and $T = 298.15$ K) and a real gas under the same pressure and temperature, which is expressed by eq 20 if the Berthelot equation of state is taken into account.

In Table 5, experimental values of liquid-phase entropy of some compounds are compared with those calculated from gas-phase data and $\Delta_{vap}H$ by first taking into account only the effect of the phase change (eq 18), denoted S^0_l*calcd, and second by correcting this value with the effect of pressure on the entropy by means of eqs 19 and 20, denoted S^0_lcalcd. Calculated entropy values including the effect of pressure are much closer to the experimental values. The highest deviations of S^0_l*calcd were observed for compounds with low vapor pressure and water. The necessity of the correction due to the effect of pressure on the entropy seems clear.

Table 7. Standard Gibbs Energy, Enthalpy, and Entropy Changes of DNHE Synthesis, DNHE Decomposition, and 2-Hexene Formation in the Liquid Phase at 298.15 K

	DNHE			1-hexene			2-hexene		
	$\Delta_r H^0_{(l),298.15}$	$\Delta_r S^0_{(l),298.15}$	$\Delta_r G^0_{(l),298.15}$	$\Delta_r H^0_{(l),298.15}$	$\Delta_r S^0_{(l),298.15}$	$\Delta_r G^0_{(l),298.15}$	$\Delta_r H^0_{(l),298.15}$	$\Delta_r S^0_{(l),298.15}$	$\Delta_r G^0_{(l),298.15}$
	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
$\Delta_r H^0_{(l)}$ constant	−8.5 ± 0.2	15.2 ± 0.5	−13.0 ± 0.4	84 ± 16	121 ± 82	46 ± 26	−9.9 ± 1.3	3 ± 3	−11 ± 2
$\Delta_r H^0_{(l)}$ as $f(T)$	−9.5 ± 0.2	12.5 ± 1.1	−13.2 ± 0.1	81 ± 16	127 ± 35	45 ± 9	−8.9 ± 1.3	6 ± 7	−11 ± 1
theor[a]	−11.9	13.0	−15.8	31	65	11.3	−9.6	−9.6	−7

[a] Computed from data given in Table 4.

In Table 5 the liquid-phase entropy corrected with the pressure factors for DNPE is also presented. In a previous work,[8] S^0_l for DNPE was calculated without considering the effect of pressure. There, it was already pointed out that it was probably an underestimation, especially when compared with the value calculated from experimental equilibrium data. In fact, S^0_l for DNPE presented in Table 5 is close to the value proposed in the previous work (473.7 ± 3.1 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) obtained from experimental results.

In Table 6, values of I_K, I_H, and a, b, c, and d for each reaction studied are shown. Values of the standard molar enthalpy, entropy, and free energy change of the three reactions at 298.15 K determined for $\Delta_r H^0_{(l)}$ assumed to be constant and for $\Delta_r H^0_{(l)}$ variable with temperature are gathered in Table 7.

As can be seen, experimental values for DNHE formation did not differ much from the theoretical data computed from enthalpy and entropy of formation of the compounds involved in the reaction. The closest value was obtained when the enthalpy of reaction was considered to be variable with temperature. The low value of $\Delta_r H^0_{(l)}$ explains what was observed experimentally: K_a^{DNHE} was slightly temperature sensitive. From $\Delta_r H^0_{(l)}$ values in Table 7 and $\Delta_f H^0_{(l)}$ values of 1-hexanol and water in Table 4, $\Delta_f H^0_{(l)}$ values for DNHE at 298.15 K can be obtained: −(477.6 ± 0.8) $\text{kJ}\cdot\text{mol}^{-1}$ if $\Delta_r H^0_{(l)}$ was considered to be constant and −(478.6 ± 0.8) $\text{kJ}\cdot\text{mol}^{-1}$ if it was variable with temperature. These values were lower by less than 1 % than that estimated by the improved Benson group-additive method[17] (−481.1 $\text{kJ}\cdot\text{mol}^{-1}$), which proves to be very useful in predicting $\Delta_f H^0_{(l)}$ for such ethers.

Following the same reasoning, the liquid-phase entropy for DNHE could be computed from the experimental results of $\Delta_r S^0_{(l)}$ presented here, and the experimental $S^0_{(l)}$ values of water and 1-hexanol shown in Table 4: (520.1 ± 0.5) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ if assumed constant with temperature and (517.4 ± 0.5) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ if considered temperature dependent. This last value is the same as the value computed from gas-phase $S^0_{(g)}$ predicted by the Benson method and then corrected by means of eq 17, taking into account the effect of pressure.

Experimental values of $\Delta_r H^0_{(l)}$ for the decomposition of DNHE to 1-hexanol and 1-hexene differed considerably from the theoretical values. Furthermore, the accuracy of this value was low, which was probably due to the small activities of 1-hexene throughout the experiments. However, $\Delta_r H^0_{(l)}$ experimental values of the isomerization of 1-hexene to 2-hexene were very close to the theoretical values.

Conclusions

The dehydration of 1-hexanol to DNHE and water proved to be slightly exothermic with an enthalpy change of reaction of −(9.5 ± 0.2) $\text{kJ}\cdot\text{mol}^{-1}$ at 298.15 K (−(8.5 ± 0.2) $\text{kJ}\cdot\text{mol}^{-1}$ if $\Delta_r H^0_{(l)}$ was assumed to be constant over the temperature range). From the experimental results, thermochemical data of DNHE formation could be computed, obtaining a $\Delta_f H^0_{(l)}$ of −(478.6 ± 0.8) $\text{kJ}\cdot\text{mol}^{-1}$ (−(477.6 ± 0.8) $\text{kJ}\cdot\text{mol}^{-1}$if considered to be constant with temperature) and a $S^0_{(l)}$ of (517.4 ± 0.5) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ((520.1 ± 0.5) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ if considered to be constant with temperature). $\Delta_f H^0_{(l)}$ estimated by a modified Benson method was very close to the experimental values. Estimations of $S^0_{(l)}$ from $S^0_{(g)}$ showed that in this reaction system the correction factor concerning the pressure change was completely significant.

The decomposition of DNHE to 1-hexene and 1-hexanol proved to be endothermic, whereas the isomerization of 1-hexene to 2-hexene was exothermic.

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