Experimental and Theoretical Study of Chemical Equilibria in the Reactive Systems of Acetals Synthesis

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S *Supporting Information*

ABSTRACT: The chemical equilibria of acetals of acetaldehyde reactive systems (with methanol, ethanol, and *n*-butanol to form 1,1-dimethoxyethane, 1,1-diethoxyethane, and 1,1-dibuthoxyethane, respectively) were studied in the temperature range (293−333 K) in the liquid phase. The three reactive systems exhibit a strong nonideal behavior in the liquid phase. The knowledge of the activity coefficients is required to obtain the thermodynamic equilibrium constants K_a. The activity coefficients were estimated by the modified UNIFAC method, which already includes the parameters for the acetal group. The reaction enthalpies for the three acetalizations in the liquid phase were obtained from the temperature dependences of the corresponding thermodynamic equilibrium constants. These values were compared to those obtained by high-level ab initio calculations of the reaction participants using the Gaussian 03 program package. Absolute electronic energy values of the molecules have been obtained using G3(MP2) level. Using these results, calculated equilibrium constants and enthalpies of reaction of the acetals synthesis in the liquid phase based on the principles of statistical thermodynamics are found to be in acceptable agreement with the data obtained from the thermochemical measurements.

1. INTRODUCTION

Acetals are being investigated as green oxygenates for diesel blending, aiming to reduce particle matter emissions, to facilitate the combustion of the final products without decreasing the ignition quality, and even improving the cetane number (see Table 1).[1] One promising fuel additive is 1,1-dibutoxyethane (DBE, Scheme 1). DBE is a diesel cetane number enhancer (see Table 1), which should have a minimum value of 51 according to the European Standards (EN 590, 2009). In terms of physical properties, the kinematic viscosity at 25 °C is 1.239 cSt,[2] normal boiling point of about 188 °C, and specific gravity of 0.8300 at 25 °C.[3] Another acetal, 1,1-diethoxyethane (DEE, Scheme 2), has reduced the particulate matter and NO_x emissions by 34.6% and 3.2%, respectively, from fuel combustion, when added 10% into diesel fuel, decreasing additionally the net contribution of CO_2 emissions by 6.4%.[4] 1,1-Dimethoxyethane (DME, Scheme 3) was stated to be usable as a cetane enhancer, but its boiling point (101 °C) may be too low for that purpose; moreover, and similarly to DEE, its flash point is also expected to be too low.[5]
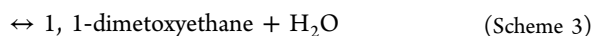
2*n*-butanol-1 + acetaldehyde

 ↔ 1, 1-dibutoxyethane + H_2O (Scheme 1)
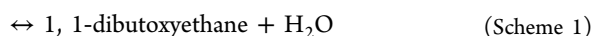
2ethanol-1 + acetaldehyde ↔ 1, 1-dietoxyethane + H_2O

             (Scheme 2)

2methanol-1 + acetaldehyde

 ↔ 1, 1-dimetoxyethane + H_2O (Scheme 3)

Table 1. Cetane Number of Different Acetals and Blends[1]

substance	cetane number	fuel	cetane number
CDF-I[a]	55	CDF-I[a]	55
DEE	44	DEE/CDF-I mixture (50/50% by volume)	53
DBE	105	DBE/CDF-I mixture (20/80% by volume)	58
DBB[b]	105	DBB[b]/CDF-I mixture (50/50% by volume)	65

[a]Commercial diesel Fuel I: ASTM 975, Type 2D produced by BP AG, Hamburg, Germany. [b]1,1-Dibutoxybutane.

Acetals synthesis involves a liquid phase reversible reaction between an alcohol and an aldehyde, catalyzed in acid medium, having water as byproduct (see Schemes 1−3). The purpose of this Article is to explore the thermodynamic limits of such reactions to further optimize the reaction conditions. Some studies report the equilibrium constants measured in the reactive mixtures for DBE,[6] DEE,[7,8] and DME,[9,10] and from its temperature dependence the reaction enthalpy $\Delta_r H_m^\circ(\text{liq})$ was derived for each reaction. In these works, the activity coefficients where evaluated by the UNIFAC method,[11] where the missing contribution for the acetal group was modeled by two ether groups. In this work, the thermodynamic equilibrium constants are recalculated using the more recent modified UNIFAC parameters,[12,13] where the contribution for acetal group is already defined, and consequently the reactions enthalpies are recalculated. To prove the validity of the procedure used, these data on $\Delta_r H_m^\circ(\text{liq})$ are compared to those calculated from the experimental enthalpies of formation of the pure reacting species according to Hess's Law. For this purpose, the enthalpy of formation of DBE was determined by combustion calorimetry. For the additional validation of the equilibrium studies and the UNIFAC calculations, we used the quantum chemical calculations. A possibility of prediction of equilibrium yields and equilibrium constants with the help of ab initio calculations was tested by using of the G3(MP2) method from the Gaussian 03 program package.

2. EXPERIMENTAL PROCEDURE

2.1. Materials. Samples of 1,1-dimethoxyethane, 1,1-diethoxyethane, acetaldehyde, methanol, ethanol, and n-butanol were of commercial origin (Sigma-Aldrich). GC analyses of the as-purchased samples of these chemicals gave purities >99% in agreement with their specifications. The degree of purity was determined using a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. The carrier gas (nitrogen) flow was 7.2 dm^3 h^{-1}. 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. The standard temperature program of the GC was T = 323 K for 180 s followed by a heating rate of 10 K min^{-1} to T = 523 K. 1,1-Dibutoxyethane was produced in a batch reactor from n-butanol using as catalyst the ion-exchange resin Amberlyst-15. After reaching chemical equilibrium, the quaternary mixture comprising n-butanol, acetaldehyde, DBE, and water was subjected to vacuum distillation to obtain DBE with high purity (99%, on molar basis). To remove the traces of n-butanol and of water, the sample was subjected to a further preconditioning procedure. After filling of the U-shaped saturator with the sample, the carrier gas with the flow rate of 1−2 dm^3 h^{-1} streams through the system at an arbitrary temperature (usually 20−30 °C). The degree of removing of water could not be monitored by GC with flame-ionization detector used in the current study. To prove the absence of water traces in the sample, numerous samples were taken consequently in the course of the sample flushing. After the amount of compound collected in the cold trap (determined by GC analysis) within an exact definite time became constant, the sample was considered to be ready for vapor pressure measurements. The final water content in the samples for thermochemical studies was measured by KF titration and taken into account by the data treatment.

2.2. Chemical Equilibrium Study in the Liquid Phase. The chemical equilibrium of acetaldehyde with n-butanol, ethanol, and methanol to produce DBE, DEE, and DME, respectively, was studied previously.[6,8,9] The thermodynamic equilibrium constants in terms of liquid activities were recalculated, using the more recent modified UNIFAC parameters used, where the acetal group is already defined. The experimental molar fractions at equilibrium in the liquid phase (x_i), the liquid phase activity coefficients, the equilibrium ratios (K_x and K_γ), and the equilibrium constants (K_{eq}) are listed in Tables 2−4, for the DBE, DEE, and DME systems, respectively.

Table 2. Experimental Equilibrium Compositions and Equilibrium Constants for DBE[6]

T (K)	293.15	303.15	313.15	323.15
x_A	0.40720	0.42078	0.43979	0.45274
x_B	0.16090	0.16742	0.17362	0.17915
x_C	0.21595	0.20590	0.19330	0.18406
x_D	0.21595	0.20590	0.19330	0.18406
K_x	1.74797	1.43019	1.11269	0.92258
γ_A	0.92140	0.95920	0.98840	1.01040
γ_B	0.68970	0.79960	0.89490	0.98170
γ_C	2.90720	2.87220	2.83530	2.76720
γ_D	5.77430	5.49590	5.20200	4.92260
K_γ	28.6693	21.4567	16.8706	13.5916
K_{eq}	50.11	30.69	18.77	12.54

Table 3. Experimental Equilibrium Compositions and Equilibrium Constants for DEE[8]

T (K)	293.15	303.15	313.15	333.15
x_A	0.38618	0.39303	0.40289	0.42345
x_B	0.15828	0.16476	0.16989	0.18057
x_C	0.22777	0.22110	0.21361	0.19799
x_D	0.22777	0.22110	0.21361	0.19799
K_x	2.19785	1.92070	1.65459	1.21065
γ_A	0.93449	0.97576	1.01002	1.06242
γ_B	0.70404	0.81602	0.91223	1.05599
γ_C	2.80313	2.79916	2.77834	2.68938
γ_D	3.37671	3.31326	3.23495	3.05895
K_γ	15.6319	11.7264	9.6730	6.9112
K_{eq}	34.36	22.52	16.00	8.37

2.3. Combustion Calorimetry. An isoperibol bomb calorimeter was used for the measurement of the energy of combustion of DBE. In the present study, we used commercially available polyethylene bulbs (NeoLab, Heidelberg) of 1 cm^3 volume as the sample container. Results from combustion experiments are given in Table S1 (Supporting Information). The detailed procedure has been described previously.[14] The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none of these substances were detected. The energy equivalent of the calorimeter ε_{calor} = 14 875.04 ± 1.0 J K^{-1} was determined with a standard reference sample of benzoic acid (sample SRM 39j, N.I.S.T.). Correction for nitric acid formation was based on the titration with 0.1 mol dm^{-3} NaOH (aq). The atomic weights used were those recommended by the IUPAC Commission.[15] The sample masses were reduced to vacuum, taking into consideration their density values (see Table S2). For converting the energy of the actual bomb process to that of

Table 4. Experimental Equilibrium Compositions and Equilibrium Constants for DME[9]

| T (K)	293.15	303.15	313.15	323.15	333.15
x_A	0.31666	0.32680	0.32718	0.35637	0.36824
x_B	0.13838	0.15565	0.15584	0.15870	0.16038
x_C	0.27248	0.25877	0.25849	0.24246	0.23569
x_D	0.27248	0.25877	0.25849	0.24246	0.23569
K_x	5.35109	4.02825	4.00494	2.91674	2.55439
γ_A	0.85738	0.88049	0.92614	0.96162	0.99528
γ_B	0.56677	0.64540	0.70916	0.74414	0.78715
γ_C	2.62029	2.68236	2.66445	2.72178	2.69816
γ_D	2.80997	2.83291	2.82320	2.77853	2.74235
K_γ	17.4637	15.0675	12.2154	11.0877	9.3646
K_{eq}	93.45	60.70	48.92	32.34	23.92

the isothermal process, and reducing to standard states, the conventional procedure[16] was applied. Small amounts of water and 1-butanol could not be removed from the samples prepared for thermochemical measurements. The exact amount of water, 0.27 mass percent in the sample for combustion experiment, was measured by using Karl Fischer titration. The exact amount of the residual n-butanol 2.50 mass percent in the sample for combustion experiment was measured by the GC using the method of external standard. The appropriate corrections to the masses of samples have been performed.

2.4. Energy of Combustion and Enthalpy of Formation of DBE. Results of combustion experiments on DBE are given in Table 5. The value of the standard specific energy

Table 5. Experimental Thermochemical Data at T = 298.15 K ($p°$ = 0.1 MPa) for DBE (in kJ mol^{-1})

$\Delta_c H_m^\circ$(liq)	$\Delta_f H_m^\circ$(liq)	$\Delta_l^g H_m$	$\Delta_f H_m^\circ$(g)
-6478.3 ± 2.1	-600.9 ± 2.5	58.6 ± 0.3	-542.3 ± 2.5

of combustion $\Delta_c u° = -(37\,107.7 \pm 4.3)$ J g^{-1} has been used to derive the standard molar enthalpy of combustion $\Delta_c H_m^\circ$(liq) = $-(6478.3 \pm 2.1)$ kJ mol^{-1} and the standard molar enthalpy of formation in the liquid state $\Delta_f H_m^\circ$ (liq) = $-(600.9 \pm 2.5)$ kJ mol^{-1} based on the reaction:

$$C_{10}H_{22}O_2 + 14.5 O_2 = 10 CO_2 + 11 H_2O \qquad (1)$$
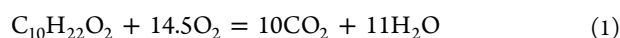
$\Delta_f H_m^\circ$(liq) DBE has been obtained from the enthalpic balance according to eq 2:

$$\Delta_f H_m^\circ(\text{liq, } C_{10}H_{22}O_2)$$
$$= 10 \times \Delta_f H_m^\circ(\text{g, } CO_2) + 11 \times \Delta_f H_m^\circ(\text{liq, } H_2O)$$
$$- \Delta_c H_m^\circ(\text{liq, } C_{10}H_{22}O_2) \qquad (2)$$

where the molar enthalpies of formation of H_2O(l) and CO_2(g) were taken from literature, as recommended by CODATA.[17] The total uncertainty of $\Delta_f H_m^\circ$(liq) was calculated according to the guidelines presented by Olofsson.[18] The uncertainty assigned to $\Delta_f H_m^\circ$(liq) is twice the overall standard deviation and 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 H_2O and CO_2.

2.5. Vapor Pressure Measurements on DBE. The enthalpy of vaporization and vapor pressures of the liquid DBE were determined by using the method of transference in a saturated N$_2$-stream. The method has been described before[20,21] and has proved to give results being in excellent agreement with

other established techniques for determining vapor pressures of pure substances and enthalpies of vaporization from the temperature dependence of the vapor pressure. The sample was mixed with glass beads (to provide surface that is sufficient enough for the vapor−liquid equilibration) and placed in a glass saturator having a length of 20 cm and a diameter of 0.5 cm. A stream of an inert gas (N$_2$) was passed through the U-tube at constant temperature (±0.1 K) under saturation conditions at each temperature. The transported material was collected in a cold trap at 243 K and quantified chromatographically using the method of an external standard. We used in this work the tetradecane as standard. Saturation vapor pressures p_i were calculated according to the ideal gas law from the amount of product m_i collected within a definite period of time:

$$p_i = m_i \cdot R \cdot T_a / V \cdot M_i \qquad (3)$$

where M_i is the molar mass of the compound i. The total volume of the system $V = V_{N2} + V_i$ consists from the volume V_{N2} of transporting gas and the volume contribution V_i to the gaseous phase of the compound i under study. It is apparent that $V_{N2} \gg V_i$. The volume V_{N2} was calculated from the flow rate and time measurements. The flow rate is measured with the soap bubble meter at ambient temperature T_a. R is the universal gas constant.

To the best of our knowledge, these compounds have been studied for the first time. Vapor pressures of DBE measured in this work and enthalpies of vaporization (Table S3) were treated with eqs 4 and 5, respectively.

$$R \cdot \ln p_i^{sat} = a + \frac{b}{T} + \Delta_l^g C_p \cdot \ln\left(\frac{T}{T_0}\right) \qquad (4)$$

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p \cdot T \qquad (5)$$

The value of $\Delta_l^g C_p$ = 108.9 J/(mol K) was calculated using a procedure suggested by Chickos and Acree.[19] Experimental value of the isobaric molar heat capacities of liquid, C_p^1, of DBE required for $\Delta_l^g C_p$ calculations was not found in the literature. Values of C_p^1 = 378.1 J/(mol K) were assessed using the group contribution method.[19] Vapor pressures obtained by the transpiration method are reliable within 1−3% according to test measurements with the alkanols.[20] The accuracy of vapor pressures is mostly governed by reproducibility of the analytical procedure used for the determination of the transported mass m_i, and a contribution due to uncertainties of other experimental parameters given in eq 1 is negligible.[20] Our experimental data were approximated with eq 4 as follows:

$$\ln(p^{\text{sat}}/\text{Pa}) = \frac{341.52}{R} - \frac{91\,049.79}{(R \cdot T/\text{K})} - \frac{108.9}{R} \ln\left(\frac{T/\text{K}}{298.15}\right)$$

The vapor pressure data for DBE over a wide range of temperature 306−464 K were determined by use of a modified Ramsay−Young apparatus.[3] The data presented there were also treated using eqs 4 and 5, and $\Delta_l^g H_m$(298.15 K) =57.8 ± 0.2 kJ mol^{-1} is in acceptable agreement with our result from transpiration method $\Delta_l^g H_m$(298.15 K) = 58.6 ± 0.3 kJ mol^{-1} (see Table S3). Slight disagreement of vaporization enthalpies $\Delta_l^g H_m$(298.15 K) from Ramsay−Young and transpiration could be partly accounted for very long extrapolation of ebulliometric data to the reference temperature. However, the values of absolute vapor pressures for DBE reported by Conner and coauthors[3] are generally in very good agreement with our new measurements (see Figure 1) except for the lowest
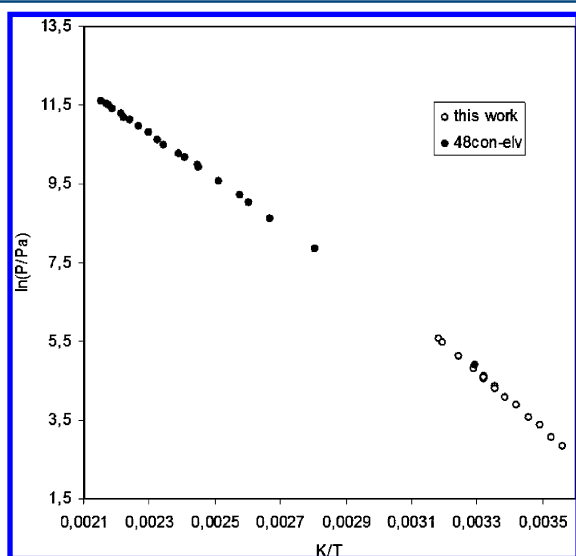
Figure 1. Experimental vapor pressures of the DBE: comparison between result of this work and those from Conner et al. (1948).

experimental point. Yet it is well-known that the ebulliometric measurements at low temperatures are not reliable enough due to difficulties with equilibration.

2.6. Calculation of the Gaseous Enthalpy of Formation of DBE. The value of vaporization enthalpy of DBE, derived in this work (Table S3), has been used together with the results from combustion experiments (Table S1) for further calculation of the gaseous standard enthalpy of formation, $\Delta_f H_m^\circ$(g), at 298.15 K. The resulting value of $\Delta_f H_m^\circ$(g) = −(542.3 ± 2.5) kJ mol^{-1} of DBE is given in the last column of Table 5.

2.7. Computations. Standard ab initio molecular orbital calculations were performed with the Gaussian 03 revision 04 series of programs.[22] Energies were obtained at the G3(MP2) level of theory. G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second rows of the periodic chart based on ab initio molecular orbital theory. A modification of G3 theory that uses reduced orders of Moller−Plesset perturbation theory is G3(MP2) theory.[23] The Gaussian-4 (G4) composite model[24] combines high-level correlation/moderate basis set calculations with lower level correlation/larger basis set calculations to approximate the results of a more expensive calculation. The composite energy is obtained from results using CCSD(T), MP4, MP2, and HF

calculations with progressively larger basis sets, and including first-order spin−orbit corrections for atoms and molecules (SO), zero-point energy corrections (ZPE), and an empirical higher level correction (HLC) that depends on the number of paired and unpaired electrons. The G4 model contains new features, energies, use of density functional geometries, an extension of the G3Large basis set with additional polarization on the first two rows referred to as G3LargeXP, and a slightly modified higher level correction. G4 theory gives an average absolute deviation of 3.5 kJ mol^{-1}[24] on the G3/05 experimental test set of energies, a considerable improvement over G3 theory (4.7 kJ mol^{-1}),[23] and well within the target accuracy of 4−5 kJ mol^{-1}.[25] No corrections for internal rotors have been taken into account. The enthalpy values of at T = 298.15 K were evaluated according to standard thermodynamic procedures.[26]

3. RESULTS AND DISCUSSION

3.1. Calculation of Enthalpy of Formation of Acetals. Conformational analysis of 1,1-dimethoxyethane, 1,1-diethoxyethane, and 1,1-dibutoxyethane is important for a correct calculation of their enthalpy of formation $\Delta_f H_m^\circ$(g). According to conformational analysis, the most stable conformer for each compound was obtained and used for calculation of enthalpies of formation on the basis of the atomization reaction (AT) and isodesmic reactions (see Table S4).

As can be seen from this table, enthalpies of formation calculated by using G3(MP2) from the atomization reaction and the four isodesmic reactions for acetals are in good agreement.

3.2. Validation of Enthalpy of Formation of Acetaldehyde. In this work, we need enthalpy of formation of acetaldehyde in the liquid phase to apply Hess's Law to reactions 1−3. Enthalpy of formation of acetaldehyde has been obtained as $\Delta_f H_m^\circ$(l) = −(196.4 ± 1.5) kJ mol^{-1} by Wiberg et al.[27] by measuring the enthalpies of reaction of the carbonyl compounds and of the alcohols with lithium triethylborohydride in triglyme using reaction calorimetry. Using the enthalpy of vaporization $\Delta_l^g H_m$(298.15 K) = (26.1 ± 0.3) kJ mol^{-1} selected by Majer and Svoboda,[28] enthalpy of formation of acetaldehyde in the gaseous phase can be calculated as $\Delta_f H_m^\circ$(g) = −(170.3 ± 1.5) kJ mol^{-1}. The latter value is in disagreement with the older result $\Delta_f H_m^\circ$(g) = −(166.1 ± 0.5) kJ mol^{-1} measured by the hydrogenation calorimetry in the gaseous phase performed by Dolliver et al.[29] da Silva et al.[30] suggested that this later value was correct, as it provided an accurate enthalpy for formaldehyde from an isodesmic reaction scheme. Recently, Carstenson et al.[31] have calculated the formation enthalpy of acetaldehyde to be −170.5 kJ mol^{-1} from CBS-QB3 calculations. Later, da Silva and Bozzelli[32] suggested the value $\Delta_f H_m^\circ$(g) = −(166.2 ± 0.7) kJ mol^{-1} as the average from values calculated using the G3, G3B3, and CBS-APNO theoretical methods, in conjunction with bond-isodesmic work reactions. Thus, the data set for enthalpies of formation of acetaldehyde seems to be in disarray from experimental and theoretical points of view. In this work, we have performed additional quantum-chemical calculations of enthalpy of formation of acetaldehyde using G3(MP2) and G4 methods (see Table S5). With help of atomization procedure, we have calculated the enthalpy of formation of acetaldehyde in the gaseous phase as −165.3 kJ mol^{-1} from G3(MP2) and −166.5 kJ mol^{-1} from G4 method. It has turned out that all quantum chemical calculations (except for CBS-APNO Carstenson et al.[31]) strongly support the older calorimetric result $\Delta_f H_m^\circ$(g) =

Table 6. Comparison of the Thermodynamic Functions $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$ of the Reactions in the Liquid Phase from $\ln K_x = a + b \cdot (T/K)^{-1}$ and $\ln K_a = a + b \cdot (T/K)^{-1}$

		kJ mol^{-1}			J mol^{-1} K^{-1}
reaction	$T_{av}{}^a$	$\Delta_r H_m^\circ$ (equilibrium)	$\Delta_r H_m^\circ$ (calorimetry)^d	$\Delta_r H_m^\circ$(liq) (eq 6)^e	$\Delta_r S_m^\circ$
1	308	$-17.1 \pm 1.3^{b,6}$			-53.6 ± 4.2
		$-14.7 \pm 1.1^{c1,6}$	-40.1 ± 2.6	-47.0 ± 5.0	-38.9 ± 3.7
		$-36.7 \pm 1.1^{c2,6}$			-92.8 ± 3.5
2	313	$-12.2 \pm 1.2^{b,7,8}$			-34.9 ± 3.9
		$-9.8 \pm 0.5^{c1,7,8}$	-31.7 ± 0.8	-40.1 ± 5.0	-32.0 ± 1.7
		$-28.5 \pm 1.1^{c2,7,8}$			-67.9 ± 3.5
3	313	$-14.6 \pm 3.9^{b,9}$			-36.1 ± 12.4
		$-17.7 \pm 3.8^{c1,9}$	-35.4 ± 1.0	-41.7 ± 5.0	-34.8 ± 12.2
		$-27.2 \pm 3.3^{c2,9}$			-55.2 ± 10.4
	298	$-15.0 \pm 5.6^{b,10}$			-36.8 ± 18.7
		$-17.5 \pm 5.3^{c1,10}$			-33.7 ± 17.7

^{a}The average temperature of the equilibrium study. It was assumed[18] that the enthalpy of reaction changes on passing from the average temperature of the experimental range to $T = 298$ K are negligible within the boundaries of the uncertainties. ^{b}Derived from the temperature dependence of K_x. ^{c}Derived from the temperature dependence of K_a calculated with the old (c1) and new (c2) UNIFAC parameters. ^{d}Calculated from the enthalpies of formation of the reaction participants measured by combustion calorimetry at $T = 298.15$ K. ^{e}Calculated direct using H_{298} of the reaction participants obtained from G3(MP2) according to eq 6.

$-(166.1 \pm 0.5)$ kJ mol^{-1} measured directly in the gaseous phase by Dolliver et al.[29] The required in this work enthalpy of formation of acetaldehyde in the liquid phase $\Delta_f H_m^\circ(l) = -(192.2 \pm 0.6)$ kJ mol^{-1} we calculated from a combination of the experimental gaseous enthalpy data from Dolliver et al.[29] and the vaporization enthalpy recommended by Majer and Svoboda.[28]

3.3. Comparison of the Reaction Enthalpies Obtained from Equilibrium Studies and from Calorimetry. Reactions of dialkylacetals synthesis (reactions 1−3) were studied in the temperature range from 293 to 333 K, and the standard enthalpies of these reactions in the liquid phase were derived indirectly from the slope of $\ln K_a$ versus $1/T$-plots or $\ln K_x$ versus $1/T$-plots (see Table 6). The validity of the reaction enthalpies 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 pure reactions participants according to Hess's law. Experimental data on $\Delta_f H_m^\circ$(liq) necessary for such a comparison are available in the literature (see Table S6). These data were used to calculate independently $\Delta_r H_m^\circ{}_{(calorimetry)}$ of the acetal synthesis reactions in the liquid phase (see Table 6), for reaction 1:

$$\Delta_r H_m^\circ(liq)_{(calorimetry)}$$
$$= \Delta_f H_m^\circ(liq)_{(DBE)} + \Delta_f H_m^\circ(liq)_{(H2O)}$$
$$- 2 \times \Delta_f H_m^\circ(liq)_{(BuOH)} - \Delta_f H_m^\circ(liq)_{(AcA)}$$
$$= -(40.1 \pm 2.6) \text{ kJ mol}^{-1}$$

Comparison of equilibrium and calorimetric results of reactions 1−3 is given in Table 6. Calculated values of the $\Delta_r H_m^\circ{}_{(calorimetry)}$ for reactions 1−3 are in quite good agreement with those derived from the chemical equilibrium studies, confirming their thermodynamic consistency.

3.4. Comparison of the Reaction Enthalpies Obtained from Equilibrium Studies and from ab Initio Calculations. In our recent work,[35] we established a remarkable ability of the G3(MP2) ab initio method to predict gaseous enthalpies of organic carbonates accurately. An additional test to establish the validity of the experimental and calculation

procedures presented in this Article provides the comparison of the reaction enthalpies of reactions 1−3 obtained from experimental calorimetric studies and from ab initio calculations. Using the G3(MP2) procedure, the standard reaction enthalpies, $\Delta_r H_m^\circ(g)$, of reactions 1−3 in the ideal gaseous phase at 298.15 K were calculated (see Table 7). The values of

Table 7. Thermodynamic Functions $\Delta_r G_m^\circ$, $\Delta_r H_m^\circ$, and $\Delta_r S_m^\circ$ of Reactions 1−3 at $T = 298$ K Calculated Using G3(MP2)

	kJ mol^{-1}		J mol^{-1} K^{-1}
reaction	$\Delta_r G_m^\circ(g)$	$\Delta_r H_m^\circ(g)$	$\Delta_r S_m^\circ(g)$
1	-15.4	-75.1	-200.1
2	-10.4	-67.7	-192.5
3	-9.0	-66.4	-192.6

$\Delta_r H_m^\circ(g)$ are related to the standard reaction enthalpies, $\Delta_r H_m^\circ$(liq), in the liquid state by

$$\Delta_r H_m^\circ(liq) = \Delta_r H_m^\circ(g)_{G3MP2} - \sum_i \nu_i \Delta_l^g H_{mi} \qquad (6)$$

where $\Delta_l^g H_{mi}$ are the molar enthalpies of vaporization of the pure compounds i at the reference temperature. The latter values for compounds involved in reactions 1−3 are well established and are available in the literature (see Table S6). Enthalpies of reaction $\Delta_r H_m^\circ(g)_{G3(MP2)}$ calculated directly from enthalpies of reaction participants using G3(MP2) are given in Table 7 (column 3). Enthalpies of reactions 1−3 $\Delta_r H_m^\circ(liq)_{G3(MP2)}$ in the liquid phase calculated according to eq 6 are listed for comparison with experimental values in Table 6 (column 5). The calculated values of the $\Delta_r H_m^\circ(liq)_{G3(MP2)}$ for reactions 1−3 are systematically of about 7 kJ mol^{-1} more negative than those calculated according to Hess's law from calorimetric data (Table 6, column 4) and those from the chemical equilibrium studies (Table 6, column 3). However, taking into account the uncertainties of the G3(MP2) of ± 5 kJ mol^{-1}, the agreement with the both experimental techniques seems to be still acceptable.

3.5. Additive Calculations of Thermodynamic Properties of Acetals. The group-additivity methods[33,34,36−38] serve as a valuable tool for many scientists and engineers whose work

Table 8. Thermochemical Data at T = 298.15 K ($p°$ = 0.1 MPa) in kJ/mol

compounds	$\Delta_f H_m°$(liq)	GA	Δ	$\Delta_l^g H_m$	GA	Δ	$\Delta_f H_m°$(g)	GA	Δ
1,1-DME	−420.0 ± 0.8[34]	−419.1	−0.9	32.6 ± 0.2[34]	30.8	1.8	−387.9 ± 0.9	−389.7	−1.8
1,1-DEE	−493.1 ± 0.4[34]	−493.1	0.0	39.1 ± 0.3[34]	39.2	−0.1	−454.0 ± 0.5	−454.0	0.0
1,1-DBE	−600.9 ± 2.5	−598.2	−2.7	58.6 ± 0.3	58.2	0.4	−542.3 ± 2.5	−540.8	−1.5

involves thermodynamic characterization of elementary and overall reaction processes. Benson's group additivity method[38] seems to have the most widespread acceptance at present, and the overall best record for reliability of estimation techniques. In this work, we have adjusted the Benson procedure to the acetals using experimental data collected in Verevkin et al.[34] and using modification for branched species suggested by Roganov and coauthors.[33] The summary of increments required for prediction enthalpies of formation and enthalpies of vaporization is collected in Table S7. As can be seen from Table 8, the experimental and calculated values using the group-additivity (GA) method are consistent within the experimental uncertainties.

4. CONCLUSIONS

In this work, the reaction enthalpies of three acetalization reactions for the synthesis of DBE, DEE, and DME in the liquid phase were obtained from experimental (chemical equilibrium, and calorimetry) and theoretical (ab initio calculations) studies.

The experimental enthalpies of the reactions (in liquid phase) determined from calorimetric studies were in acceptable agreement with those derived from the chemical equilibrium experiments (using the modified UNIFAC model, which includes the acetal group). Using the quantum chemical method (composite method G3(MP2)), the reaction enthalpies in the liquid phase were predicted with reasonable accuracy. We established a consistent set of thermodynamic data for the liquid and the gaseous states as well as the data on vaporization enthalpies for the typical acetalization reactions of industrial importance.

ASSOCIATED CONTENT

S **Supporting Information**

Additional tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.
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