Thermochemistry of Ionic Liquid-Catalyzed Reactions. Experimental and Theoretical Study of Chemical Equilibria of Isomerization and Transalkylation of *tert*-Butylbenzenes

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The chemical equilibrium of mutual interconversions of *tert*-butylbenzenes was studied in the temperature range 286 to 423 K using chloroaluminate ionic liquids as a catalyst. Enthalpies of five reactions of isomerization and transalkylation of *tert*-butylbenzenes were obtained from temperature dependences of the corresponding equilibrium constants in the liquid phase. Molar enthalpies of vaporization of methyl-*tert*-butylbenzenes and 1,4-di*tert*-butylbenzene were obtained by the transpiration method and were used for a recalculation of enthalpies of reactions and equilibrium constants into the gaseous phase. Using these experimental results, ab initio methods (B3LYP and G3MP2) have been tested for prediction thermodynamic functions of the five reactions under study successfully. Thermochemical investigations of *tert*-butylbenzenes available in the literature combined with experimental results have helped to resolve contradictions in the available thermochemical data for *tert*-butylbenzene and to recommend consistent and reliable enthalpies of formation for this compound in the liquid and the gaseous state.

1. Introduction

The Friedel−Crafts alkylations of aromatic compounds are among the most important processes in the chemical industry.[1] Traditionally, these types of reactions are carried out in the presence of Lewis acid catalysts, such as $AlCl_3$ or $AlBr_3$, or hazardous Brønsted acids such as HF or H_2SO_4, which inevitably leads to a series of environmental problems as well as operational difficulties in product separation and purification. Recently, a few of examples of the Friedel−Crafts alkylations of aromatic compounds with alkenes have been reported to proceed in ionic liquids (ILs), a kind of novel and promising solvent for synthetic chemistry.[2,3] It is known that these alkylation reactions could be carried out either directly using chloroaluminate ionic liquids as catalysts[4,5] or employing an ionic liquid catalytic system containing scandium triflate.[6]

It is well established[2,7,8] that chloroaluminate ionic liquids exhibit a wide range of Lewis acidity depending on the molar ratio of reactants. In general, the acid−base properties of this catalytic system are described by the equilibrium:

$$2AlCl_4^- \leftrightarrow Al_2Cl_7^- + Cl^-$$

where $[Al_2Cl_7]^-$ is the Lewis acid and Cl^- is the Lewis base. For example, a $(1 + 1)$ mixture of quaternary ammonium chloride and $AlCl_3$ affords the tetrachloroaluminate anion $([AlCl_4]^-)$ which is referred to as being neutral and is not active as a Friedel−Crafts catalyst. In contrast, the $(1 + 2)$ mixture of quaternary chloride and $AlCl_3$ forms the $[Al_2Cl_7]^-$ anion which is strongly acidic and was shown to be very active in Friedel−Crafts alkylations and acylations.[2,3] A crucial advantage of the chloroaluminate ILs is their adjustable Lewis acidity where substantial variations in acidity can be effected simply by varying the molar ratio of the two

components and can be used to produce task specific selective catalysts.

These ionic liquids can function as both a catalyst and a solvent for acid catalyzed processes such as the Friedel−Crafts alkylation of benzene with long chain α-olefins which is used industrially for the manufacture of more than two million tons per annum of linear alkylbenzenes worldwide.[1] The products are the precursors of the corresponding alkylbenzene sulfonates which are widely used as surfactants. The potential to retrofit existing installations with the ionic liquid catalyst offers enormous benefits with regard to reduced catalyst consumption, ease of product separation, and elimination of caustic quenching associated with catalyst leaching.[3] In this context, a systematic study of the mutual interconversion of alkylbenzenes in the presence of chloroaluminate ILs could contribute to modification of chemical processes that will have high yields and generate only small quantities of hazardous waste streams.

The purpose of this work is two-fold. First, we aim to study chemical equilibrium of *tert*-butyl-substituted benzenes in three separate model systems using chloroaluminate ionic liquids (see Figure 1). In our earlier studies[9,10] of chemical interconversions of *tert*-butyl-substituted benzenes in System I we observed very rapid deactivation of the $AlBr_3$ or $AlCl_3$ catalyst culminating in low selectivity and tar formation even at room temperature. However, the use of chloroaluminate imidazolium-, quaternary ammonium-, and phosphonium-based ionic liquids as both solvent and catalyst as described in this study should allow much more mild and selective conditions in comparison to either $AlCl_3$ or $AlBr_3$ catalysts. Systematic studies of the temperature dependences of equilibrium constants of the reactions 1−5 provide a reliable knowledge of their thermodynamic functions (reaction enthalpies, $\Delta_r H_m^\circ$, and reaction entropies, $\Delta_r S_m^\circ$) according to the The Second Law Method.[11]

Second, we wish to resolve the contradiction existing between available[10] experimental enthalpy of formation, $\Delta_f H_m^\circ$, of *tert*-butylbenzene and a recent theoretical value of $\Delta_f H_m^\circ$ obtained[13]

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System I

$$m\text{-di-}t\text{-Bu-Bz} + \text{Bz} = 2\times t\text{-Bu-Bz} \tag{1}$$

$$p\text{-di-}t\text{-Bu-Bz} = m\text{-di-}t\text{-Bu-Bz} \tag{2}$$

System II

$$t\text{-Bu-Bz} + \text{T} = m\text{-}t\text{-Bu-T} + \text{Bz} \tag{3}$$

$$p\text{-di-}t\text{-Bu-T} = m\text{-}t\text{-Bu-T} \tag{4}$$

System III

$$3,5\text{-di-Me-}t\text{BuBz} + \text{Bz} = t\text{Bu-Bz} + 1,3\text{-di-Me-Bz} \tag{5}$$
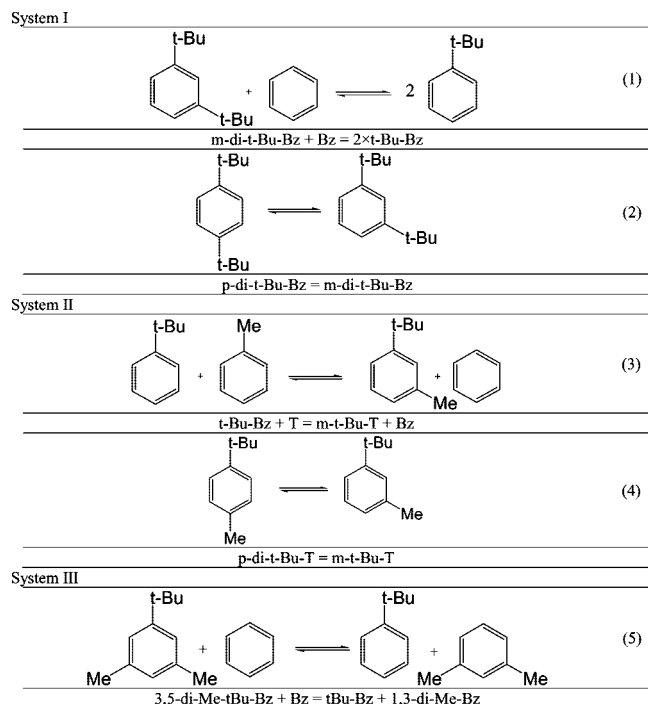
Figure 1. Three systems of transalkylation and isomerization reactions of *tert*-butyl-substituted benzenes studied.

from ab initio calculations using B3LYP method. Extended high level density functional theory calculations have recently been carried out for a series of benzene derivatives.[13] On the basis of these calculations, the performance of different theoretical schemes aimed at reproducing substituent effects on $\Delta_f H_m^\circ$ has been assessed.[13] According to this study,[13] the experimental value for $\Delta_f H_m^\circ$ of *tert*-butylbenzene suggests this needs to be revised. In the present work we have measured enthalpies of reactions 1, 3, and 5 in the ionic liquid catalyzed systems. We have used these results to derive new independent $\Delta_f H_m^\circ$ of *tert*-butylbenzene according to Hess's Law. Additionally, in this work we have also performed high-level ab initio calculations for all reaction participants (see Figure 1) using one of the DFT methods B3LYP/6–31G(d,p) and the composite G3MP2 method.[14] New experimental results, as well as the G3MP2 calculations, have strongly supported the earlier available[10,12] experimental data on $\Delta_f H_m^\circ$ of *tert*-butylbenzene.

2. Experimental Procedures

2.1. Materials. Samples of alkylbenzenes were of commercial origin (Acros, 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$^3\cdot$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 internal 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$\cdot$min^{-1} to T = 523 K.

Chloroaluminate ionic liquids were prepared according to a general procedure.[7] The catalyst, anhydrous AlCl$_3$, was slowly added to imidazolium-, quaternary ammonium-, or phosphonium-based ionic liquids. The mixture was stirred at 426 K until the catalyst completely dissolved.

2.2. Chemical Equilibrium Study in the Liquid Phase. Equilibrium transalkylations of *tert*-butyl-substituted benzenes according to reactions 1–5 were studied in the temperature range 286–423 K. Glass vials with a screwed cap top were two-thirds filled with an initial liquid mixture of *tert*-butyl-substituted benzenes with benzene, toluene, or *m*-xylene. Catalytic amounts (~30% weight of the mixture) of chloroaluminate ionic liquids, AlCl$_3$, FeCl$_3$, and Amberlyst-15 were added, and the system was thermostatted at a given temperature with an uncertainty of ±0.1 K and periodically shaken. Two phases were formed when using chloroaluminate ILs (the upper phase was colorless, but the lower phase was slightly brown). At measured time intervals the vial was rapidly cooled in ice and opened and a sample for GC analysis taken from the upper liquid phase using a syringe. After the vial was thermostated at the original temperature, the procedure was repeated. Sampling was continued until no further change of the compositions was observed, indicating that the chemical equilibrium was established. Analysis of the samples taken during equilibration in presence of AlCl$_3$ or FeCl$_3$ occurred after dilution with water, extraction of the water solution with the diethyl ether, and drying over Na$_2$SO$_4$. In the case of chloroaluminate ionic liquids samples, the upper organic level was not found to contain any significant amount of the ionic liquid catalyst; therefore, samples were analyzed without pretreament using GC. The equilibrium ratios K_x of reactions 1–5 in the liquid phase were determined as a ratio of mole fractions x_i of the reaction participants. Mole fractions x_i at equilibrium in the liquid phase, and values of K_x, are listed in Tables 1–3.

2.3. Vapor Pressure Measurements of *tert*-Butyl-Substituted Benzenes. Transpiration Method. Vapor pressures of 3-*tert*-butyltoluene, 4-*tert*-butyltoluene, and 1,4-di-*tert*-butylbenzene were determined using the method of transpiration in a saturated nitrogen stream. The method has been described previously[15–17] and has proved to give results that are 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 from the temperature dependence of the vapor pressure. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-shaped tube having a length of 20 cm and a diameter of 0.5 cm. Glass beads with a diameter of the glass spheres of 1 mm provide surface large enough for rapid vapor−liquid equilibration. At constant temperature (±0.1 K) a nitrogen stream was passed through the U-tube and the transported amount of material was collected in a cold trap. The flow rate of the nitrogen stream was measured using a soap bubble flow meter and was optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The amount of condensed substance was determined by GC analysis using an external standard (n-decane). The saturation vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of the product collected within a definite period of time. Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance i of interest is valid, values of p_i^{sat} were calculated with equation:

$$p_i^{\text{sat}} = m_i R T_a / V M_i; \quad V = V_{N2} + V_i; \quad (V_{N2} \gg V_i) \tag{6}$$

where R = 8.314472 J$\cdot$K$^{-1}\cdot$mol^{-1}, m_i is the mass of the transported compound, M_i is the molar mass of the compound, and V_i is the volume contribution to the gaseous phase. V_{N2} is the volume of the carrier gas, and T_a is the temperature of the

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TABLE 1: System I: Experimentally Determined Composition of Equilibrium Mixtures and K_x Values in the Liquid Phase[a]

catalyst	T	n	x_{Bz}	$x_{t-Bu-Bz}$	$x_{m-di-t-BuBz}$	$x_{p-di-t-BuBz}$	$x_{1,3,5-tri-tBuBz}$	$K_{x(1)}$	$K_{x(2)}$
AlCl$_3$	293	6	0.5174	0.4176	0.0349	0.0301	-	9.7	1.16
[P$_{666\ 14}$][Cl]:[AlCl$_3$] = (1:2)	293	5	0.6612	0.3103	0.0150	0.0135	-	9.7	1.11
[N$_{8881}$][Cl]:[AlCl$_3$] = (1:2)	293	3	0.5178	0.4152	0.0357	0.0313	-	9.3	1.14
[[BMIM][Cl]:[AlCl$_3$] = (1:1.1)	293	5	0.5254	0.4125	0.0331	0.0290	-	9.8	1.14
[BMIM][Cl]:[AlCl$_3$] = (1:2)	293	4	0.5220	0.4154	0.0333	0.0293	-	9.9	1.14
[BMIM] [Cl]:[AlCl$_3$] = (1:2)	313	5	0.5225	0.4161	0.0333	0.0281		10.0	1.19
[BMIM][Cl]:[AlCl$_3$] = (1:2)	323	5	0.6035	0.3545	0.0233	0.0187	-	8.9	1.25
[BMIM][Cl]:[AlCl$_3$] = (1:2)	343	5	0.5955	0.3609	0.0241	0.0195	-	9.1	1.24
[BMIM][Cl]:[AlCl$_3$] = (1:2)	363	5	0.5836	0.3717	0.0252	0.0195		9.4	1.29
Amberlyst-15	403	5	0.1272	0.5023	0.1998	0.1535	0.0172	9.9	1.30
Amberlyst-15	423	10	0.1700	0.5287	0.1696	0.1209	0.0108	9.7	1.40

[a] T is temperature of investigation in K; n is number of determinations of composition within the time of equilibrium study; x_i is the mole fraction measured chromatographically.

TABLE 2: System II: Experimentally Determined Composition of Equilibrium Mixtures and K_x Values in the Liquid Phase[a]

catalyst	T	n	x_{Bz}	x_T	$x_{t-Bu-Bz}$	$x_{m-di-t-Bu-T}$	$x_{p-di-t-Bu-T}$	$x_{m-di-t-Bu-Bz}$	$x_{p-di-t-Bu-Bz}$	$K_{x(4)}$	$K_{x(2)}$	$K_{x(1)}$	$K_{x(3)}$
[BMIM]Cl:AlCl$_3$ = (1:2)	286	3	0.3406	0.2566	0.2574	0.0735	0.0298	0.0215	0.0206	2.47	1.04	9.0	0.38
	303	4	0.4533	0.2231	0.2203	0.0503	0.0263	0.0145	0.0122	1.91	1.19	7.4	0.46
	313	5	0.4050	0.2457	0.2291	0.0647	0.0269	0.0157	0.0129	2.41	1.22	8.3	0.47
	323	4	0.4766	0.2638	0.1788	0.0456	0.0203	0.0081	0.0068	2.25	1.19	8.3	0.46
	333	3	0.3397	0.2502	0.2620	0.0734	0.0310	0.0234	0.0203	2.37	1.15	8.6	0.38
	343	5	0.3662	0.2904	0.2378	0.0567	0.0245	0.0127	0.0117	2.31	1.09	12.2	0.30
	353	3	0.3416	0.2561	0.2561	0.0719	0.0311	0.0235	0.0197	2.31	1.19	8.2	0.37
	363	4	0.3402	0.2681	0.2492	0.0720	0.0290	0.0228	0.0187	2.48	1.22	8.2	0.37
AlCl$_3$	286	5	0.4067	0.2993	0.2050	0.0488	0.0201	0.0103	0.0098	2.43	1.05	10.0	0.32
	303	3	0.3997	0.2981	0.2104	0.0502	0.0204	0.0110	0.0102	2.46	1.08	10.1	0.32
	313	4	0.4538	0.2683	0.1939	0.0464	0.0203	0.0095	0.0078	2.29	1.22	8.7	0.40
	323	5	0.4255	0.2983	0.1961	0.0446	0.0180	0.0093	0.0082	2.48	1.13	9.7	0.32
	333	5	0.3955	0.2983	0.2129	0.0497	0.0220	0.0113	0.0103	2.26	1.10	10.1	0.31
	343	4	0.4214	0.2986	0.1980	0.0445	0.0191	0.0099	0.0085	2.33	1.16	9.4	0.32
	353	5	0.4172	0.2994	0.2007	0.0442	0.0202	0.0100	0.0083	2.19	1.20	9.7	0.31
	363	3	0.4069	0.3005	0.2046	0.0480	0.0202	0.0103	0.0095	2.38	1.08	10.0	0.32
[HMIM]Cl:AlCl$_3$ = (1:2)	313	3	0.2603	0.1460	0.3972	0.0672	0.0272	0.0530	0.0491	2.47	1.08	11.4	0.30
	323	3	0.2643	0.1425	0.4087	0.0531	0.0268	0.0543	0.0503	1.98	1.08	11.6	0.24
	333	3	0.2596	0.1425	0.3946	0.0681	0.0290	0.0550	0.0512	2.35	1.07	10.9	0.31
	343	3	0.2913	0.1476	0.3827	0.0574	0.0253	0.0494	0.0463	2.27	1.07	10.2	0.30

[a] T is temperature of investigation in K; n is number of determinations of composition within the time of equilibrium study; x_i is the mole fraction measured chromatographically.

TABLE 3: System III: Experimentally Determined Composition of Equilibrium Mixtures and K_x Values in the Liquid Phase[a]

catalyst	T	n	x_{Bz}	x_T	$x_{1.3-di-Me-Bz}$	$x_{t-Bu-Bz}$	$x_{m-t-Bu-T}$	$x_{p-t-Bu-T}$	$x_{3.5-di-Me-t-Bu-Bz}$	$x_{m-di-t-Bu-Bz}$	$x_{p-di-t-Bu-Bz}$	$K_{x(4)}$	$K_{x(2)}$	$K_{x(1)}$	$K_{x(3)}$	$K_{x(5)}$
[BMIM]Cl: AlCl$_3$ = (1:2)	286	5	0.3315	0.0202	0.2080	0.3216	0.0084	0.0038	0.0429	0.0322	0.0314	2.21	1.03	9.7	0.43	4.7
	303	3	0.3223	0.0116	0.2035	0.3485	0.0055	0.0025	0.0448	0.0312	0.0301	2.20	1.04	12.1	0.44	4.9
	313	4	0.2800	0.0108	0.2109	0.3394	0.0051	0.0023	0.0469	0.0545	0.0501	2.22	1.09	7.5	0.39	5.5
	333	3	0.2953	0.0147	0.2049	0.3340	0.0066	0.0031	0.0442	0.0516	0.0456	2.13	1.13	7.3	0.40	5.2
	343	4	0.3050	0.0184	0.2123	0.3238	0.0074	0.0038	0.0415	0.0472	0.0406	1.95	1.16	7.3	0.38	5.4
	353	5	0.3139	0.0197	0.2154	0.3327	0.0076	0.0038	0.0410	0.0365	0.0294	2.00	1.24	9.7	0.36	5.6
	363	4	0.3267	0.0206	0.2145	0.3202	0.0077	0.0037	0.0393	0.0323	0.0350	2.08	0.92	9.7	0.38	5.3
FeCl$_3$	287	6	0.2403		0.1888	0.3972			0.0441	0.0680	0.0616		1.10			
	323	6	0.3988		0.1483	0.3151			0.0350	0.0543	0.0485		1.12			

[a] T is temperature of investigation in K; n is number of determinations of composition within the time of equilibrium study; x_i is the mole fraction measured chromatographically.

soap bubble meter. The volume of the carrier gas V_{N2} was determined from the flow rate and the time measurement.

3. Results

3.1. Equilibrium Constants, Reaction Enthalpies, and Reaction Entropies. The experimental results of chemical equilibria study of systems I, II, and III are listed in Tables 1−3. The experimental values of K_x for all reactions measured in this work are only slightly changed with the temperature. Experimental

values of K_x for reactions 1−5 were approximated as a function of temperature by the linear equation ln $K_x = a + b(T/K)^{-1}$ using the method of least-squares. The slopes of these lines when multiplied by the gas constant afford the standard enthalpies of these reactions, $\Delta_r H_m^\circ$. The intercept of these lines when multiplied by the gas constant afford the standard entropies of this reaction $\Delta_r S_m^\circ$. Numerical resultsare presented in Table 4. The errors in the thermodynamic functions from equilibrium study are given by the standard deviations for the meaningful level 0.05.

TABLE 4: Thermodynamic Functions $\Delta_r H_m^{\circ}$ and $\Delta_r S_m^{\circ}$ of the Reactions 1−5 in the Liquid Phase, and Temperatute Dependences $\ln K_x = a + b \cdot (T/K)^{-1}$

reaction	$\langle T \rangle$,[a] K	a	b	$\Delta_r H_m^{\circ}$, kJ·mol^{-1}	$\Delta_r S_m^{\circ}$, J·mol^{-1} K^{-1}
1	364.5	2.3	−2.7	0.1 ± 0.4	18.8 ± 1.3
2	364.5	0.76	−199.1	1.7 ± 0.5	6.3 ± 1.5
3	324.5	−1.6	191.4	−1.6 ± 1.5	−13.3 ± 4.6
4	324.5	0.66	51.7	−0.4 ± 0.8	5.5 ± 2.4
5	324.5	2.2	−182.4	1.5 ± 1.0	18.4 ± 1.0

[a] The average temperature of the equilibrium study. [b] The values of the enthalpies $\Delta_r H_m^{\circ}$ and entropies $\Delta_r S_m^{\circ}$ of reactions 1−5 were derived for the average temperatures given in the column 2. It was assumed that the enthalpies of the reaction hardly change on passing from the average temperature of the experimental range to $T = 298$ K.

3.2. Vapor Pressure and Vaporization Enthalpies of *tert*-Butyl-Substituted Benzenes. Experimental vapor pressures of *tert*-butyl-substituted benzenes measured in this work were treated with eqs 7 and 8, respectively

$$R \ln p_i^{sat} = a + \frac{b}{T} + \Delta_l^g C_p \ln\left(\frac{T}{T_0}\right) \qquad (7)$$

$$\Delta_l^g H_m(T) = -b + \Delta_l^g C_p T \qquad (8)$$

where p_i^{sat} is vapor pressure, a and b are adjustable parameters (Table 5), T_0 is an arbitrarily chosen reference temperature (T_0 is 298.15 K in this work), and $\Delta_l^g C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phase. Values of $\Delta_l^g C_p$ were calculated from isobaric molar heat capacity C_p^l of *tert*-butyl-substituted benzenes using the group contribution method of Chickos and Acree.[18] In order to assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i^{sat}) = f(T^{-1})$ using the method of least-squares. The uncertainty in the enthalpy of vaporization was assumed to be identical with the average deviation of experimental $\ln(p_i^{sat})$ values from this linear correlation (uncertainties in values of $\Delta_l^g C_p$ are not taken into account). This experimental and calculation procedure has been validated with measurements of vapor pressures of n-alkanols.[17] Vapor pressures derived from the transpiration method were reliable to 1−3%.

Our new vapor pressures conducted over a wide temperature range are in close agreement with our earlier measurements, where *tert*-butyltoluenes were studied in a narrower temperature range.[10] (see Figure 1 and 2, Supporting Information). Vapor pressure over liquid 1,4-di-*tert*-butylbenzene was studied for the first time. Values of vaporization enthalpies of *tert*-butyl-substituted benzenes derived with help of eq 8 are given in Table 5.

4. Discussion

4.1. General Aspects. 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 Enthalpies Measurements). Combustion calorimetry exhibits the conventional method for measuring $\Delta_f H_m^{\circ}$ of stable species in the condensed state (solid or liquid). The accuracy of measurements of the energy released in a combustion calorimeter is close to ±0.01%, with the reliability of the derived enthalpy of combustion highly dependent on the purity of the sample. Enthalpies of formation of *tert*-butyl-substituted benzenes (relevant to the present work) measured using the combustion calorimetry[10,12] are collected in the Table S1 (see Supporting Information). Moreover, there were some concerns regarding the reliability of the enthalpy of formation $\Delta_f H_m^{\circ}(liq)$ of *tert*-butylbenzene measured by Prosen et al.,[12] because only a final value (see Table 6) was reported without providing details about combustion procedure. However, the recent combustion experiments performed in our laboratory have confirmed the earlier calorimetric result (see Table 6). An additional proof of the $\Delta_f H_m^{\circ}(liq)$ of *tert*-butylbenzene could be obtained from the temperature dependences of equilibrium constants of the reactions 1, 3, and 5 according to the The Second Law Method.

The Second Law Method (Equilibrium Constant Measurements). For a general chemical reaction in the liquid phase, e.g.,

$$A + B \rightarrow C + D \qquad (9)$$

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

$$K = \frac{a_C a_D}{a_A a_B} \qquad (10)$$

From the van't Hoff relation

$$d \ln K/dT = \Delta_r H_m^{\circ}/RT^2 \qquad (11)$$

the slope of a plot $R(\ln K)$ vs $1/T$ gives the standard enthalpy of reaction $\Delta_r H_m^{\circ}$ if the temperature dependence of the equilibrium constant K is known. From the enthalpy of reaction 9, the enthalpy of formation of a particular reaction participant can be determined provided that the values of $\Delta_f H_m^{\circ}$ for 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 affected by purity requirements in comparison to direct calorimetric methods because the equilibrium ratio K_x is measured, which is defined for the reaction (9) as:

$$K_x = \frac{x_C x_D}{x_A x_B} \qquad (12)$$

where x_i is the mole fraction of the component i. K_x defined by eq 12 is related to K in eq 10 by

$$K = K_x \frac{\gamma_C \gamma_D}{\gamma_A \gamma_B} \qquad (13)$$

where γ_i is the activity coefficient of component i. As a rule, values of γ_i depend on the mixture composition. However, according to our earlier experiences[9,10] the ratio of γ_i values in eq 13 is very close to unity. Thus, for the reactions 1−5 under study in the present work, the equilibrium ratios K_x calculated from mole fractions of reaction participants are nearly equal to the true thermodynamic constant K. Hence,

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TABLE 5: Vapor Pressures p and $\Delta_f^g H_m$ of *tert*-Butyl-Substituted Benzenes Obtained by the Transpiration Method

T, K[a]	m, mg[b]	$V(N_2)$,[c] dm^3	flow, dm$^3\cdot$h^{-1}	p, Pa[d]	$(p_{exp} - p_{calc})$, Pa	$\Delta_f^g H_m$, kJ$\cdot$mol^{-1}
1-Methyl-4-*tert*-butylbenzene						

$$\Delta_f^g H_m (298\ K) = (52.22 \pm 0.14)\ kJ\cdot mol^{-1}$$

$$\ln(p/\text{Pa}) = \frac{282.11}{R} - \frac{72883.64}{R\cdot(T/K)} - \frac{69.3}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T, K	m, mg	$V(N_2)$	flow	p, Pa	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$
273.5	2.36	2.950	4.92	13.96	0.6	53.93
276.5	3.33	3.277	4.92	17.51	0.1	53.72
278.6	2.57	2.130	4.92	20.70	-0.1	53.57
280.7	2.49	1.721	4.92	24.63	-0.1	53.43
283.8	2.57	1.393	4.92	31.29	-0.2	53.22
288.3	3.16	1.202	1.13	44.30	-0.5	52.91
293.2	3.22	0.845	1.13	63.84	-1.1	52.56
298.2	2.85	0.517	1.13	91.80	-1.0	52.22
303.1	2.76	0.366	1.13	125.2	-5.1	51.88
308.0	3.09	0.282	1.13	181.6	0.3	51.54
308.0	2.76	0.255	1.02	179.6	-1.6	51.54
310.0	3.14	0.255	1.02	204.3	-2.0	51.40
313.0	4.35	0.282	1.13	254.0	5.1	51.19
315.0	4.35	0.255	1.02	282.8	0.6	51.05
317.9	24.80	1.216	4.56	335.7	-1.6	50.85
318.0	5.19	0.255	1.02	336.9	-1.4	50.85
319.9	6.12	0.260	1.02	389.4	8.1	50.71
322.9	7.42	0.263	1.13	466.3	13.2	50.51

<div align="center">1-Methyl-3-*tert*-butylbenzene</div>

$$\Delta_f^g H_m(298\ K) = (51.09 \pm 0.32)\ kJ\cdot mol^{-1}$$

$$\ln(p/\text{Pa}) = \frac{280.24}{R} - \frac{71756.25}{R\cdot(T/K)} - \frac{69.3}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T, K	m, mg	$V(N_2)$	flow	p, Pa	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$
274.4	2.06	1.919	2.02	19.49	0.6	52.74
278.4	2.63	1.784	2.02	26.22	-0.2	52.47
283.0	2.78	1.313	2.02	37.03	-1.1	52.15
288.2	3.36	1.044	2.02	55.31	-1.4	51.79
293.4	3.16	0.640	2.02	84.05	0.9	51.43
298.1	2.78	0.404	2.02	116.8	1.0	51.10
302.7	3.20	0.337	2.02	160.2	1.9	50.78
308.2	3.20	0.236	2.02	228.0	1.3	50.40
313.5	2.61	0.141	2.02	309.9	-5.8	50.03
318.5	3.62	0.141	2.02	429.2	2.9	49.69

<div align="center">1.4-Di-*tert*-butylbenzene</div>

$$\Delta_f^g H_m(298\ K) = (61.39 \pm 0.26)\ kJ\cdot mol^{-1}$$

$$\ln(p/\text{Pa}) = \frac{296.06}{R} - \frac{82972.76}{R\cdot(T/K)} - \frac{72.4}{R}\ln\left(\frac{T/K}{298.15}\right)$$

T, K	m, mg	$V(N_2)$	flow	p, Pa	$(p_{exp} - p_{calc})$	$\Delta_f^g H_m$
354.2	13.57	0.469	4.27	376.7	0.3	57.33
359.0	12.91	0.344	4.27	488.2	0.2	56.98
356.5	12.80	0.390	4.27	426.2	-0.6	57.17
364.3	13.38	0.265	4.27	654.2	10.5	56.60
361.8	12.89	0.297	4.27	564.1	-1.4	56.78
366.5	15.00	0.269	4.27	723.6	3.6	56.44
369.2	12.20	0.192	4.27	823.1	-1.1	56.25
366.6	10.62	0.192	4.27	716.3	-7.3	56.43
372.1	13.94	0.192	4.27	940.4	-10.2	56.04
374.2	15.37	0.192	4.27	1036.4	-15.7	55.88
376.5	17.37	0.192	4.27	1171.5	-2.5	55.72
383.3	23.99	0.192	4.27	1617.2	9.3	55.23
379.8	20.41	0.192	4.27	1376.2	6.2	55.48
381.8	22.36	0.192	4.27	1507.6	5.7	55.33

[a] Temperature of saturation. [b] Mass of transferred sample condensed at T = 243 K. [c] Volume of nitrogen used to transfer the mass m of sample. [d] Vapor pressure at temperature T calculated from m and the residual vapor pressure at T = 243 K.

reaction enthalpy, $\Delta_r H_m^\circ$, can be easily calculated from the temperature dependence of the ratios K_x (see Table 4).

4.2. Two Validation of the Experimental Enthalpy of Formation, $\Delta_f H_m^\circ$(liq), of *tert*-Butylbenzene. Reactions of *tert*-butyl-substituted benzenes transalkylations 1, 3, and 5 were studied in the temperature range (286–423) K, and the standard enthalpies of these reactions, $\Delta_r H_m^\circ$, in the liquid phase were derived indirectly from the slope of ln K_x vs $1/T$ plots (see Table 4). These $\Delta_r H_m^\circ$ values can be used to calculate enthalpy of formation, $\Delta_f H_m^\circ$(liq), of *tert*-butylbenzene using Hess's Law. Experimental data on $\Delta_f H_m^\circ$(liq) of other participants of reactions 1, 3, and 5 necessary for such a calculation are available in the literature[10,20] (see Table S1, Supporting Information). These data

were used to calculate independently $\Delta_f H_m^\circ$(liq) of *tert*-butylbenzene in the liquid phase (e.g., for reaction 1):

$$\Delta_f H_m^\circ(liq)_{\text{tert-butylbenzene}} =$$

$$1/2[\Delta_r H_m^\circ(liq)\Delta_f H_m^\circ(liq)_{1,3-\text{di-tert-butylbenzene}} +$$

$$\Delta_f H_m^\circ(liq)_{\text{benzene}}] = -(71.3 \pm 1.1)kJ \cdot mol^{-1}$$

The results of similar calculations for the reactions 3 and 5 and comparison with experimental values obtained from combustion calorimetry is given in the Table 6. As can be seen, the values of $\Delta_f H_m^\circ$(liq)$_{(\text{tert-butylbenzene})}$ calculated according to the Second Law Method are in close agreement within

TABLE 6: Compilation of Experimental Values of the Enthalpy of Formation: $\Delta_f H^{\circ}_m$(liq) of *tert*-Butylbenzene and Methyl-*tert*-butylbenzenes in the Liquid State at 298 K (in kJ·mol^{-1})

	reaction	$\Delta_f H^{\circ}_m$(liq)	ref
tert-butylbenzene	combustion	-70.7 ± 1.2	12
	combustion	-71.9 ± 0.7	10
	1	-71.3 ± 0.9	this work
	3	-71.5 ± 1.9	this work
	5	-70.6 ± 1.6	this work
		-71.2 ± 0.5	average
1-methyl-4-*tert*-butylbenzene	combustion	-109.7 ± 0.9	12
	combustion	-109.1 ± 1.7^a	34
		-109.4 ± 1.4	average
1-methyl-3-*tert*-butylbenzene	combustion	-105.5 ± 1.7^a	34
	3	-109.4 ± 1.8	this work
	4	-110.1 ± 1.2	this work
		-109.8 ± 1.5	average^b

^{a} Derived from the gaseous enthalpy of formation reported in the ref 34 with help of vaporization enthalpy measured in the present work (Table 5). ^{b} Result from the ref 34 was not taken into account.

TABLE 7: Results of Calculations of the Enthalpies of Reaction, $\Delta_r H^{\circ}_m$, Entropies of Reaction, $\Delta_r S^{\circ}_m$, and Gibbs Energies of Reaction, $\Delta_r G^{\circ}_m$, in the Gaseous Phase at 298 K

reaction	G3MP2			DFT		
	$\Delta_r G^{\circ}_m$	$\Delta_r H^{\circ}_m$	$\Delta_r S^{\circ}_m$	$\Delta_r G^{\circ}_m$	$\Delta_r H^{\circ}_m$	$\Delta_r S^{\circ}_m$
1	0.40	0.62	0.74	-2.80	-1.33	4.93
2	-0.36	-0.85	-1.64	3.54	1.80	-5.84
3	2.27	0.45	-6.10	1.57	0.41	-3.89
4	-0.03	-0.19	-0.54	0.62	0.40	-0.74
5	-2.68	0.03	9.09	-0.75	-0.55	0.67

the boundaries of their experimental uncertainties. These values are also in excellent agreement with those obtained according to the First Law Method, confirming the thermodynamic consistency of the experimental procedures applied in the present work. Taking into account the very close agreement of the available experimental data, the average value $\Delta_f H^{\circ}_m$(liq)$_{(tert-butylbenzene)} = -(71.2 \pm 0.5)$ kJ·mol^{-1} given in the Table 6 could be recommended for the further thermodynamic calculations.

5. Quantum Chemical Calculations

5.1. Methods of Calculations. High level ab initio calculations have been performed on the basis of the composite G3MP2 method as well as the B3LYP method to obtain ideal gas thermodynamic functions for all alkyl-substituted benzenes involved in reactions 1−5. Standard ab initio molecular orbital calculations were performed with the Gaussian 03 Rev. 04 series of programs.[21] Energies were obtained at the B3LYP and G3MP2 level of theory. DFT calculations are known to provide accurate geometries and reasonable energies for a variety of organic compounds.[22] We have used B3LYP/6−31G(d,p) method for the calculation of the geometry parameter, ZPE values, and normal-mode frequencies.

G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second row 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 G3MP2 theory.[14] This method saves considerable computational time compared with G3 theory with some loss in accuracy; however, it is much more accurate that G2MP2 theory. For all the species included in this study, full geometry optimizations were carried out at the HF/6−31G(d) level. The corresponding harmonic vibrational frequencies were evaluated at the same level of theory to confirm that the optimized structures found correspond to potential energy minima and to evaluate the

corresponding zero-point vibrational energies, ZPE, and the thermal corrections at $T = 298$ K. ZPE values were scaled by the empirical factor 0.8929. All the minima found at the HF/6−31G(d) level were again fully reoptimized at the MP2(FULL)/6−31G(d) level. G3MP2 theory uses geometries from second-order perturbation theory and scaled zero-point energies from Hartree−Fock theory followed by a series of single-point energy calculations at the MP2/Full, QCISD(T), and MP2/GTMP2Large levels of theory (for details see ref 14). The enthalpy values at $T = 298$ K were evaluated according to standard thermodynamic procedures.[23]

5.2. Thermodynamic Functions of Reactions 1−5. In our recent work[22,24,25] we established a remarkable ability of the G3MP2 ab initio method to predict gaseous enthalpies of formation of organic compounds accurately. It is well established that chemical reactions of isomerization and transalkylation such as 1−5 are thermodynamically controlled. Thus, desired yields of goal products could be possibly predicted with help of ab initio calculations. In order to validate this procedure, the following thermodynamic functions were calculated for the gas phase reactions 1−5 using B3LYP and G3MP2 method: Gibbs energy, $\Delta_r G^{\circ}_m$, reaction enthalpy, $\Delta_r H^{\circ}_m$, reaction entropy, $\Delta_r S^{\circ}_m$. Calculated values are given in Table 7.

5.3. Comparison of Reaction Enthalpies Obtained from Equilibrium Studies and from ab Initio Calculations. Generally, the enthalpy of chemical reaction, $\Delta_r H^{\circ}_m$, is defined as the stoichiometric difference of the enthalpies of the products and educts in the pure states. An additional test to establish validity of the experimental and calculation procedures presented in this paper provides comparison of the reaction enthalpies of reactions 1−5 obtained from experimental studies and from ab initio calculations. Using the DFT and G3MP2 procedure, the standard reaction enthalpies, $\Delta_r H^{\circ}_m$(g), of the reactions 1−5 in the ideal gaseous phase at 298 K were calculated (see Tables 7 and 8).

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TABLE 8: Enthalpies of Reactions 1−5, $\Delta_r H_m^\circ$, in the Gaseous and the Liquid Phase at $T = 298$ K (in kJ·mol^{-1})

reaction	$\Delta_r H_m^\circ$(g) (DFT)	$\Delta_r H_m^\circ$(g) (G3MP2)	$\Delta_r H_m^\circ$(liq) (DFT)	$\Delta_r H_m^\circ$(liq) (G3MP2)	$\Delta_r H_m^\circ$(liq) (exp)
1	−1.3	0.6	−3.0	−1.2	0.1 ± 0.4
2	1.8	−0.9	3.6	0.9	1.7 ± 0.5
3	0.4	0.5	1.1	1.2	−1.6 ± 1.5
4	0.4	−0.2	1.5	0.9	−0.4 ± 0.8
5	−0.6	0.1	−0.4	0.3	1.5 ± 1.0

TABLE 9: Thermodynamic Function $\Delta_r G_m^\circ$ (in kJ·mol^{-1}) and Equilibrium Constants K_p and K_x of the Reactions 1−5 at $T = 298$ K

reaction	$\Delta_r G_m^\circ$ (G3MP2)	$\Delta_r G_m^\circ$ (DFT)	K_p (G3MP2)	K_p (DFT)	K_x(theor) (G3MP2)	K_x(theor)(DFT)	K_x(exp)
1	0.40	−2.80	0.9	3.1	2.3	8.4	9.5
2	−0.36	3.54	1.2	0.2	0.6	0.1	1.1
3	2.27	1.57	0.4	0.5	0.3	0.4	0.38
4	−0.03	0.62	1.0	0.8	0.8	0.6	2.3
5	−2.68	−0.75	3.0	1.4	4.6	2.1	4.9

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

$$\Delta_r H_m^\circ(\text{liq}) = \Delta_r H_m^\circ(\text{g}) - \sum_i \nu_i \Delta_l^g H_{mi} \qquad (14)$$

where $\Delta_l^g H_{mi}$ are the molar enthalpies of vaporization of the pure compounds i at the reference temperature 298 K. The latter values for compounds involved in reactions 1−5 are well established and are available in the literature[10,20,26] (see Table S1 in Supporting Information). Enthalpies of reaction $\Delta_r H_m^\circ$(g)$_{\text{DFT}}$ and $\Delta_r H_m^\circ$(g)$_{\text{G3MP2}}$ calculated directly from enthalpies of reaction participants using B3LYP and G3MP2 are given in the Tables 7 and 8. Enthalpies of reactions 1−5, $\Delta_r H_m^\circ$(liq)$_{\text{DFT}}$ and $\Delta_r H_m^\circ$(liq)$_{\text{G3MP2}}$, in the liquid phase calculated according to eq 14 are listed for comparison with experimental values in Table 8. The calculated values of the $\Delta_r H_m^\circ$(liq)$_{\text{DFT}}$ and $\Delta_r H_m^\circ$(liq)$_{\text{G3MP2}}$ for reactions 1−5 are in good agreement (within the boundaries of experimental uncertainties) with those derived from the chemical equilibrium studies. It should be stressed that we calculated values of the $\Delta_r H_m^\circ$(liq)$_{\text{DFT}}$ and $\Delta_r H_m^\circ$(liq)$_{\text{G3MP2}}$ for reactions 1−5 using enthalpies H_{298} (see Table S2, Supporting Information) of the reaction participants directly available from the ab initio protocol. In this case we are able to avoid ambiguity due to calculations leading to the enthalpies of formation, $\Delta_f H_m^\circ$(g) as described below.

5.4. Equilibrium Constants of the Reactions 1−5. The thermodynamic equilibrium constant, K_P, calculated, for example, for the gas phase reaction 1 is related to the thermodynamic constant K_x of this reaction in the liquid phase by eq 15:

$$K_x = K_P \times \frac{P_{\text{1,3-di-}tert\text{-butylbenzene},0} \times P_{\text{benzene},0}}{P_{tert\text{-butylbenzene},0}^2} \qquad (15)$$

where $P_{i,0}$ are the saturated vapor pressures of the pure components. Saturated vapor pressures for alkylbenzenes were available in the literature[19] or they were measured in the present work (see Table S1 in Supporting Information). Using the values of K_P for the gaseous reactions 1−5 calculated with help of B3LYP and G3MP2 and presented in Table 9, the thermodynamic constants K_x (theor) in the liquid phase were calculated (see Table 9). Theoretical ratios K_x for reactions 1−5 calculated using eq 15 in Table 9 and compared there with the experimental values K_x at 298 K. Theoretical values of K_x calculated at the DFT (B3LYP) and G3MP2 level are in acceptable agreement (except for reaction 1) with the experimental values. Thus, the procedure developed in this work could be practically applied for assessment of yields of isomerization and transalkylation reactions similar to reactions 1−5 studied in this work.

Following such a procedure could be recommended in general for a large scope of reactions involving alkylation and interconversion of alkylbenzenes.

5.5. Validation of Enthalpy of Formation of *tert*-Butylbenzene Using G3MP2 Calculations. The experimental enthalpies of formation, $\Delta_f H_m^\circ$(liq), of *tert*-butylbenzene determined in this work have been shown to be in good agreement with previously reported values (see Table 6). However, the recent theoretical value of $\Delta_f H_m^\circ$(g) calculated[13] with help of B3LYP method suggests that the experimental values for *tert*-butylbenzene need to be revised. In our recent work we have successfully used high-level ab initio calculations for validation of experimental enthalpies of formations of hydrocarbons,[27] ethers,[22] esters,[28] organic carbonates,[24,29] aromatic amines,[30] benzoic acids,[31] and nitrophenols.[25]

There are several schemes to convert theoretically total energies to the corresponding standard enthalpies of formation $\Delta_f H_m^\circ$(g, 298 K). The most accurate methods involve isodesmic or homodesmic reactions. In an isodesmic reaction the number of chemical bonds of each type is conserved, so the cancelation of possible errors arising from insufficient treatment of electron correlation and incompleteness of the basis set might be expected. Homodesmic reaction will lead to even more accurate results if chemical groups are also conserved in the reaction, because next nearest neighbor interactions are also conserved.

In the present work, enthalpy of formation $\Delta_f H_m^\circ$(g, 298 K) of *tert*-butylbenzene has been calculated on the basis of the 14 selected isodesmic and homodesmic reactions presented in Table 10. Using enthalpies of reactions, calculated by G3MP2, together with available[20] experimental enthalpies of formation, $\Delta_f H_m^\circ$(g, 298 K), for other reactions participants, theoretical enthalpies of formation of *tert*-butylbenzene have been calculated (see Table 10). Results calculated from isodesmic and homodesmic reactions (Table 10) are in close agreement and the average value from all 14 reactions: $\Delta_f H_m^\circ$(g, 298 K)$_{(tert\text{-butylbenzene})}$ = -(23.7 ± 1.4) kJ·mol^{-1}. Having established this theoretical value, enthalpy of formation of the liquid *tert*-butylbenzene could be estimated by the following equation:

$$\Delta_f H_m^\circ(\text{liq}) = \Delta_f H_m^\circ(\text{g})_{\text{G3MP2}} - \Delta_l^g H_m \qquad (16)$$

Reliable data for enthalpy of vaporization, $\Delta_l^g H_m$(298 K) = (47.5 ± 0.4) kJ·mol^{-1}, of *tert*-butylbenzene have been published just recently[19,26,32] (see Table S1, Supporting Information). Thus, using eq 16, enthalpy of formation of *tert*-butylbenzene, $\Delta_f H_m^\circ$(liq) = −(71.2 ± 1.5) kJ·mol^{-1} was calculated, and this value is in excellent agreement with our new result $\Delta_f H_m^\circ$(liq) = −(71.2 ± 0.5) kJ·mol^{-1} (see Table 6) recommended in this

TABLE 10: Results from G3MP2 and B3LYP/6-31G(d,p) Calculations of $\Delta_f H^\circ_m(g)$ for *tert*-Butylbenzene at 298 K (in kJ·mol^{-1})

reaction	G3MP2	DFT
tert-butylbenzene + 10 CH$_4$ = 3 C$_2$H$_4$ + 7 C$_2$H$_6$	−19.0	3.1
tert-butylbenzene + 4 CH$_4$ = 3 C$_2$H$_4$ + 3 CH$_3$=CH-CH=CH$_3$ + 4 C$_2$H$_6$	−29.2	-
tert-butylbenzene + 3 CH$_4$ = toluene + 3 C$_2$H$_6$	−25.1	12.8
tert-butylbenzene + CH$_4$ = toluene + 2-methylpropane	−26.5	−2.2
tert-butylbenzene + C$_2$H$_6$ = isopropylbenzene + C$_3$H$_8$	−24.2	−7.9
tert-butylbenzene + ethylbenzene = 2 isopropylbenzene	−23.0	−11.3
tert-butylbenzene + C$_3$H$_8$ = isopropylbenzene + methylpropane	−24.3	−15.8
tert-butylbenzene + CH$_4$ = ethylbenzene + C$_3$H$_8$	−24.7	−0.9
tert-butylbenzene + C$_2$H$_6$ = propylbenzene + C$_3$H$_8$	−24.7	−2.2
tert-butylbenzene + 6 CH$_4$ = C$_2$H$_2$ + 3 C$_2$H$_4$ + 4 C$_3$H$_8$	−19.7	−25.1
tert-butylbenzene = 3 C$_2$H$_2$ + 2 C$_2$H$_4$	−23.1	−73.3
tert-butylbenzene = n-butylbenzene	−22.8	−2.8
tert-butylbenzene = sec-butylbenzene	−22.0	6.2
tert-butylbenzene = isobutylbenzene	−23.2	10.5
average	−23.7 ± 1.4[a]	-

[a] Experimental value $\Delta_f H^\circ_m(g) = \Delta_f H^\circ_m(\text{liq}) + \Delta_g^g H_m = -71.2 + 47.5 = -23.7 \pm 0.7$ kJ·mol^{-1} was calculated using results from Table 6 and ref 10.

TABLE 11: Results from G3MP2 Calculations of $\Delta_f H^\circ_m(g)$ for 1-Methyl-3-*tert*-butylbenzene at 298 K (in kJ·mol^{-1})

reaction	G3MP2
1-methyl-3-*tert*-butylbenzene + benzene = *tert*-butylbenzene + toluene	−55.0
1-methyl-3-*tert*-butylbenzene + 11 methane = 3 ethene + 8 ethane	−56.2
1-methyl-3-*tert*-butylbenzene + benzene = ethylbenzene + isopropylbenzene	−54.2
1-methyl-3-*tert*-butylbenzene + propane = 2,2-dimethylpropane + isopropylbenzene	−55.6
1-methyl-3-*tert*-butylbenzene = 2 isopropylbenzene	−53.4
1-methyl-3-*tert*-butylbenzene = toluene + sec-butylbenzene	−53.9
atomization	−64.2
1-methyl-3-*tert*-butylbenzene = pentamethylbenzene	−61.5
average	-56.8 ± 2.8[a]

[a] Experimental value $\Delta_f H^\circ_m(g) = \Delta_f H^\circ_m(\text{liq}) + \Delta_g^g H_m = -109.8 + 51.1 = -58.7 \pm 1.4$ kJ·mol^{-1} was calculated using results from Tables 5 and 6.

work as the average value from the experimental studies. Such good agreement between experimental and theoretical G3MP2 values is valuable check of for their mutual consistency. In contrast to the success of the composite ab initio method G3MP2, our calculations of $\Delta_f H^\circ_m(g, 298\,\text{K})_{(tert\text{-butylbenzene})}$ using the DFT method B3LYP/6−31G(d,p) and the same set of reactions given in the Table 10 have shown the inacceptable spread of values over 80 kJ·mol^{-1} (see Table 10). Similar scatter was obtained using B3LYP/6−31G(d), B3LYP/6−311G(d,p), and B3LYP/6−311+G(3df,2p) calculations.[13] These results confirm a recommendation from the recent study that DFT methods have to be applied with caution, because of systematic errors, which could be traced back to the neglect of dispersion interactions in DFT.[33] At the same time, the DFT and the G3MP2 methods could be successfully applied for calculation of equilibrium constants and thermodynamic functions of reactions similar to 1−5, apparently due to cancelation of possible errors.

5.5. Validation of Enthalpies of Formation of *tert*-Butyltoluenes. The experimental enthalpies of formation, $\Delta_f H^\circ_m(g)$, of o-, m-, and p-*tert*-butyltoluenes (methyl-*tert*-butylbenzenes) were reported in ref 34 as a private communication by Dr. E. J. Prosen from National Bureau of Standards (see Table 6). These values were measured using combustion calorimetry, but, similar to *tert*-butylbenzene (as mentioned above), any details about combustion procedure, or even values of vaporization enthalpies, have never been published in the open literature. As can be seen, $\Delta_f H^\circ_m(l)$ of p-*tert*-butyltoluene from ref 34 is in excellent agreement with the recent calorimetric result.[10] In the present

work we are able to derive $\Delta_f H^\circ_m(l)$ of m-*tert*-butyltoluene from our studies of reactions 3 and 4 in the liquid phase (see Table 6) using the procedure similar to those we have applied for *tert*-butylbenzene in chapter 4.2. Two values of $\Delta_f H^\circ_m(l)$ of m-*tert*-butyltoluene from this work are in very close agreement, and we derived the average value −(109.8 ± 1.5) kJ·mol^{-1}. The disagreement with the enthalpy of formation $\Delta_f H^\circ_m(l) = -(105.5 \pm 1.7)$ kJ·mol^{-1} of m-*tert*-butyltoluene from ref 34 could be rather due to insufficient characterized purity of the sample used in ref 34. In order to get support to experimental values, enthalpies of formation $\Delta_f H^\circ_m(g, 298\,\text{K})$ of *tert*-butyltoluenes have been calculated on the basis of the eight selected isodesmic and homodesmic reactions presented in Tables 11−13. Using enthalpies of reactions, calculated by G3MP2, together with available[20] experimental enthalpies of formation, $\Delta_f H^\circ_m(g, 298\,\text{K})$, for other reactions participants, theoretical enthalpies of formation of *tert*-butyltoluenes have been calculated (see Tables 11−13). As can be seen from these tables, theoretical and experimental results for o-, m-, and p-*tert*-butyltoluenes are in very close agreement.

5.6. Strain of *tert*-Butyltoluenes. It is well established that *tert*-alkylbenzenes are strained.[10] We define the strain of a molecule as the difference between the experimental standard enthalpy of formation $\Delta_f H^\circ_m(g)$ and the calculated sum of the strain-free increments of the Benson type[10] for this molecule. All the increments necessary in this work are as follows:[10] CH$_3$[C] = −42.05 kJ·mol^{-1}; C[4C] = −1.26 kJ·mol^{-1}; C$_B$H[2C$_B$] = 13.72 kJ·mol^{-1}; C$_B$ [C, 2C$_B$] = 23.51 kJ·mol^{-1} (C$_B$ represents the aromatic C atoms). Using these group-additivity parameters and the experimental values of $\Delta_f H^\circ_m(g)$ of *tert*-butyltoluenes (Tables 10−13) derived in this research, the values of strain enthalpies $\Delta H_{m(\text{strain})} = \{\Delta_f H^\circ_m(g) - \Sigma \text{increments}\}$ of *tert*-butylbenzene (11.6 kJ·mol^{-1}), o-*tert*-butyltoluene (34.1 kJ·mol^{-1}), m-*tert*-butyltoluene (8.9 kJ·mol^{-1}), and p-*tert*-butyltoluene (10.4 kJ·mol^{-1}), have been estimated. All studied *tert*-butylbenzenes are strained. The value of $\Delta H_{m(\text{strain})} = 11.6$ kJ·mol^{-1} for the *tert*-butylbenzene has been included in each molecule studied. This value describes the intrinsic strain of the *tert*-butylbenzenes due to steric repulsions

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TABLE 12: Results from G3MP2 Calculations of $\Delta_f H_m^\circ(g)$ for 1-Methyl-4-*tert*-butylbenzene at 298 K (in kJ·mol⁻¹)

reaction	G3MP2
1-methyl-4-*tert*-butylbenzene + benzene = *tert*-butylbenzene + toluene	−54.8
1-methyl-4-*tert*-butylbenzene + 11 methane = 3 ethene + 8 ethane	−56.1
1-methyl-4-*tert*-butylbenzene + benzene = ethylbenzene + isopropylbenzene	−54.0
1-methyl-4-*tert*-butylbenzene + propane = 2,2-dimethylpropane + isopropylbenzene	−55.4
1-methyl-4-*tert*-butylbenzene + toluene = 2 isopropylbenzene	−53.2
1-methyl-4-*tert*-butylbenzene + benzene = toluene + *sec*-butylbenzene	−53.7
atomization	−64.0
1-methyl-4-*tert*-butylbenzene = pentamethylbenzene	−61.3
average	−56.6 ± 2.8[a]

[a] Experimental value $\Delta_f H_m^\circ(g) = \Delta_f H_m^\circ(liq) + \Delta_l^g H_m = -109.4 + 52.2 = -57.2 \pm 1.5$ kJ·mol⁻¹ was calculated using results from Tables 5 and 6.

TABLE 13: Results from G3MP2 Calculations of $\Delta_f H_m^\circ(g)$ for 1-Methyl-2-*tert*-butylbenzene at 298 K (in kJ·mol⁻¹)

reaction	G3MP2
1-methyl-2-*tert*-butylbenzene + benzene = *tert*-butylbenzene + toluene	−32.5
1-methyl-2-*tert*-butylbenzene + 11 methane = 3 ethene + 8 ethane	−33.8
1-methyl-2-*tert*-butylbenzene + benzene = ethylbenzene + isopropylbenzene	−31.7
1-methyl-2-*tert*-butylbenzene + propane = 2,2-dimethylpropane + isopropylbenzene	−33.2
1-methyl-2-*tert*-butylbenzene + tolyene = 2-isopropylbenzene	−31.0
1-methyl-2-*tert*-butylbenzene + benzene = toluene + *sec*-butylbenzene	−31.4
atomization	−41.8
1-methyl-2-*tert*-butylbenzene = pentamethylbenzene	−39.0
average	−34.3 ± 2.8[a]

[a] Experimental value $\Delta_f H_m^\circ(g) = -33.5 \pm 1.7$ kJ·mol⁻¹ from ref .

of methyl groups and the benzene ring attached to the quaternary carbon atom. The comparison with this strain allowed the derivation of the effects of non-nearest-neighbor interactions of the *tert*-butyl and the methyl substituents on the benzene ring directly. We calculated the differences between individual strains for each compound and the strain of *tert*-butylbenzene: *o-tert*-butyltoluene (22.5 kJ·mol⁻¹), *m-tert*-butyltoluene (−2.7 kJ·mol⁻¹), and *p-tert*-butyltoluene (−1.6 kJ·mol⁻¹). These values were interpreted as the sum of excess pairwise interactions of alkyl substituents on the benzene ring. The quantities of the pairwise interactions of methyl and *tert*-butyl substituents in the meta and para position indicated a very weak stabilization. In contrast, the interaction of the *tert*-butyl and methyl groups led to a strong destabilization of (22.5 kJ·mol⁻¹) due to sterical repulsions of the methyl groups.

6. Conclusions

Experimentally determined chemical equilibrium data of the chemical reactions involving *tert*-butyl-substituted benzenes in

the liquid phase offer to test theoretical results obtained from ab initio calculations in the gaseous phase. In particular, the results obtained for the gaseous phase demonstrate that ab initio calculation methods available today allow prediction of chemical equilibrium data in the liquid phase with good quality. The present work demonstrates the usefulness of ab initio calculations in predicting chemical equilibrium properties of reactions being of considerable technical importance.

Supporting Information Available: Thermodynamic data for compounds used in this work (Table S1); total energies at 0 K and enthalpies at 298 K (in Hartree) of the molecules studied in this work (Table S2); calculation of enthalpies of formation of di-*tert*-butylbenzenes in the liquid phase (Table S3); comparison for experimental vapor pressures of the 1-methyl-3-*tert*-butylbenzene and 1-methyl-4-*tert*-butylbenzene (Figure S1 and Figure S2). This information is available free of charge via the Internet at http://pubs.acs.org.

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