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

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The chemical equilibrium of mutual interconversions of *tert*-amylbenzenes was studied in the temperature range 286–423 K using chloroaluminate ionic liquids as a catalyst. Enthalpies of isomerization and transalkylation of *tert*-amylbenzene were obtained from temperature dependences of the corresponding equilibrium constants in the liquid phase. The molar enthalpy of formation of *tert*-amylbenzene was measured using combustion calorimetry and was also obtained by the transpiration method. Using these experimental results, high-level ab initio methods (B3LYP and G3MP2) have been successfully tested for the prediction of reaction enthalpies for the four reactions under study. New experimental results have been used to derive a strain of *tert*-amylbenzene, which is useful in any additive scheme as the non-nearest-neighbor interaction which is specific for the branched alkylbenzenes.

1. Introduction

Alkylation of benzene is an important industrial process, which is achieved by the acid-catalyzed alkylation of aromatics using AlCl_3 as a catalyst. Many conventional processes suffer from disadvantages such as the formation of aluminate waste, cumbersome product recovery, and nonreuse of the catalyst.¹ Prolonged reaction times and low yields are also other drawbacks encountered during conventional alkylation procedures. It is well established^{2,3} that chloroaluminate ionic liquids (CILs) are suitable candidates as a replacement for AlCl_3 . In general, the acid–base properties of this catalytic system are described by the equilibrium



where Al_2Cl_7^- is the Lewis acid and Cl^- is the Lewis base. A (0.5 + 0.5 mol fraction) 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. The AlCl_3 mole fraction where $x < 0.5$ affords Lewis basic and those greater than $x > 0.5$ afford Lewis acidic ionic liquids.⁴ A crucial advantage of the chloroaluminate ILs is their adjustable Lewis acidity where substantial variations in acidity ($0.5 < x < 0.75$) can be altered by varying the molar ratio of the two components and can be used to produce task specific catalysts which are molten at ambient or near ambient temperatures.³ These molten 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 linear alkylbenzenes.

It is well-known that the tertiary pentenes (amylenes) are produced by catalytic cracking of the crude oil. The yield of

the C_5 cut is about 10% by mass relative to the catalytic naphtha, and this C_5 cut contains up to 30% amylenes by mass. Separation and utilization of the tertiary pentenes into valuable chemical products such as *tert*-amylbenzene [CAS 2049-95-8] is of academic and industrial importance.⁵ In our previous study² concerning the chemical interconversions of *tert*-butyl-substituted benzenes, we established that chloroaluminate ionic liquids based on imidazolium, quaternary ammonium, and phosphonium ionic liquids are milder and more selective catalysts in comparison to either AlCl_3 or AlBr_3 . Preliminary experiments with similar mixtures containing *tert*-amylbenzene in presence of AlCl_3 and AlBr_3 revealed a very rapid and complete conversion of *tert*-amylbenzene into the more thermodynamically stable isomers: 2,2-dimethylpropylbenzene [1007-26-7] and 1,2-dimethylpropylbenzene [4481-30-5]. Mechanisms for this rearrangement have already been studied and were shown to occur only in the presence of strong Lewis acids such as AlCl_3 via a hydride abstraction process.^{5,6} In this work, we have been interested in obtaining milder reaction conditions using chloroaluminate ionic liquids as the catalyst, where the skeletal isomerization of the alkyl substituent is suppressed. Such mild and selective conditions should allow investigation of the equilibrium of interconversions of *tert*-amyl-substituted benzenes without rearrangement of the amyl side chain (see Figure 1). Synthetic alkylbenzenes are produced as complex isomeric mixtures, thus a careful study of physical–chemical and thermodynamic properties will allow optimization of the separation of industrially scaled alkyl–benzene mixtures.

This work extends our previous study² on chemical equilibrium of *tert*-alkyl-substituted benzenes using chloroaluminate ionic liquids as the catalyst with the ab initio methods (B3LYP and G3MP2) (see Figure 1). Systematic studies of the temperature dependences of equilibrium constants for the reactions 1–4 provide reliable information 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*.^{2,7} This is the first work

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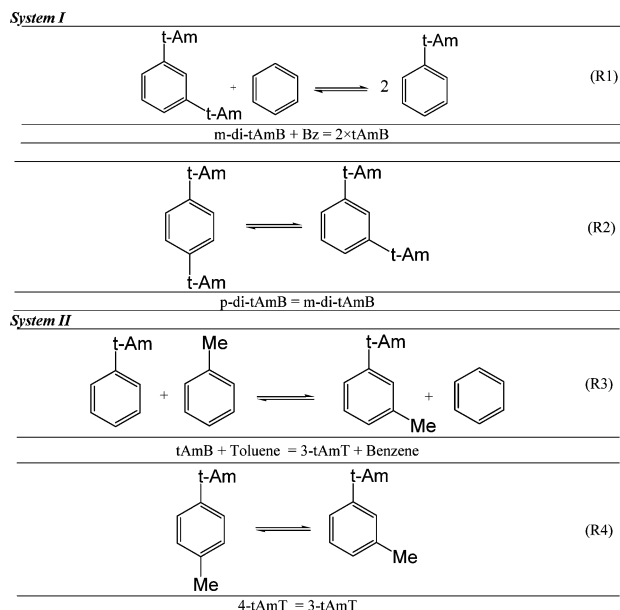


Figure 1. Two systems of transalkylation and izomerization reactions of *tert*-amyl-substituted benzenes.

that reports thermodynamic functions for the *tert*-amylbenzenes. The enthalpy of formation, $\Delta_f H_m^\circ$, of *tert*-amylbenzene in the gaseous state has been obtained from a combination of the combustion experiments with vapor pressure measurements performed by the transpiration method. 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. New experimental results have been used to derive a strain of *tert*-amylbenzene, which is useful in any additive scheme as the non-nearest-neighbor interaction which is specific for the branched alkylbenzenes.

2. Experimental Procedures

2.1. Materials. *tert*-Amylbenzene (Lancaster, mass-fraction purity of ~0.97) was purified by repeated distillation in vacuum. Gas chromatography (GC) showed no traceable amounts of impurities in the *tert*-amylbenzene after purification. The samples used for the combustion and transpiration studies were analyzed with a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionization detector. A capillary column HP-5 (stationary phase cross-linked 5% PH ME silicone) was used with a column length of 30 m, an 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 $\text{K} \cdot \text{min}^{-1}$ to $T = 523$ K.

GC and mass spectrometric analyses of samples from the equilibrium studies were analyzed with a GC-MS Agilent 19091J-433 equipped with a flame ionization detector. A capillary column HP-5 was used with a column length of 30 m, an internal diameter of 0.25 mm, and a film thickness of 0.25 μm . The standard temperature program of the GC was $T = 343$ K followed by a heating rate of 15 $\text{K} \cdot \text{min}^{-1}$ to $T = 593$ K. Identifications of the compounds of equilibrium mixtures confirmed by ^1H NMR were performed according to the library of MS data contained in the Agilent software.

Chloroaluminate ionic liquids were prepared according to a reported general procedure.⁸ The catalyst anhydrous AlCl_3 (e.g., 1.1 mol equiv) was slowly added over a 24 h period to a 1,3-dialkyl imidazolium chloride (1 mol equiv) based ionic liquid.

TABLE 1: System I: Experimentally Determined Composition of Equilibrium Mixtures and K_x -Values in the Liquid Phase (T is Temperature of Investigation in K)

catalyst	T	x_{Benzene}	$x_{s\text{-AmB}}^a$	$x_{t\text{-AmB}}$	$x_{m\text{-tAmT}}$	$x_{p\text{-tAmT}}$	$K_{x(\text{R1})}$	$K_{x(\text{R2})}$
[BMIM][Cl]:	303	0.5966	0.0489	0.3220	0.0185	0.0141	9.4	1.31
[AlCl ₃] = (1:1.1)	313	0.5456	0.0543	0.3607	0.0222	0.0171	10.7	1.30
	323	0.5724	0.0233	0.3627	0.0238	0.0177	9.7	1.34
	343	0.6237	0.0329	0.3154	0.0137	0.0143	11.7	0.95

^a *s*-AmB = 2-Methyl-3-phenylbutane (CAS 4481-30-5).

The mixture was then stirred at 426 K until the catalyst had completely dissolved resulting in a colorless or near colorless solution.

2.2. Chemical Equilibrium Study in the Liquid Phase. Equilibrium transalkylations of *tert*-amyl substituted benzenes according to reactions 1–4 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*-amyl-substituted benzenes dissolved in benzene or toluene. Catalytic amounts (~30% by weight of the mixture) of chloroaluminate ionic liquids, FeCl_3 , or 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 ionic liquids, with the upper organic phase remaining colorless and the lower ionic liquid phase darkening during the reaction. At measured time intervals, the vial was rapidly cooled in ice and opened, and a sample for GC analysis was taken from the upper liquid phase using a syringe. After thermostating the vial 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 the presence of pure AlCl_3 or FeCl_3 occurred after dilution with water, extraction of the water solution with the diethyl ether, and drying over Na_2SO_4 . In the case of chloroaluminate ionic liquid samples, the upper organic level was not found to contain any significant amount of the ionic liquid catalyst, therefore samples were analyzed without pretreatment using GC. All GC measurements were repeated twice. The equilibrium ratios K_x of reactions 1–4 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 and 2. Two systems of transalkylation and izomerization reactions of *tert*-amyl-substituted benzenes under study are presented in Figure 1. It is worse to mention that in system I only reactions 1 and 2 took place. In the system II, all reactions 1–4 have occurred.

2.3. Vapor Pressure Measurements of *tert*-Amylbenzene. Transpiration Method. Vapor pressures of *tert*-amylbenzene were determined using the method of transpiration in a saturated nitrogen stream. The method that has been described before^{9,10} has been proven to give results in excellent agreement with other established techniques for determining vapor pressures of pure substances in the range of 0.005 to ca. 10000 Pa and enthalpies of vaporization from the temperature dependence of the vapor pressure. Approximately 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 1 mm provide a 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 to reach the saturation

TABLE 2: System II: Experimentally Determined Composition of Equilibrium Mixtures and K_x Values in the Liquid Phase (T is Temperature of Investigation in K)

	T	x_{Benzene}	x_{Toluene}	$x_{\text{s-AmB}}$	x_{tAmB}	x_{sAmT}	$x_{\text{m-tAmT}}$	$x_{\text{p-tAmT}}$	$x_{\text{m-di-tAmB}}$	$x_{\text{p-di-tAmB}}$	$K_{\text{x(R1)}}$	$K_{\text{x(R2)}}$	$K_{\text{x(R3)}}$	$K_{\text{x(R4)}}$
[BMIM][Cl]:[AlCl ₃] = (1:1.1)	286	0.3504	0.3878	0.0126	0.1400	—	0.0704	0.0269	0.0058	0.0060	9.6	0.97	0.45	2.61
	303	0.4142	0.3330	0.0099	0.1450	—	0.0599	0.0254	0.0063	0.0062	8.1	1.01	0.51	2.36
	313	0.3929	0.3692	0.0118	0.1273	—	0.0638	0.0245	0.0052	0.0054	7.9	0.97	0.53	2.61
	323	0.4274	0.3442	0.0090	0.1318	—	0.0535	0.0229	0.0056	0.0055	7.2	1.02	0.50	2.34
	333	0.3857	0.3718	0.0119	0.1295	—	0.0655	0.0249	0.0053	0.0055	8.1	0.97	0.52	2.63
	343	0.3591	0.3919	0.0118	0.1335	—	0.0670	0.0256	0.0055	0.0057	8.9	0.98	0.46	2.62
	353	0.3835	0.3694	0.0122	0.1321	—	0.0664	0.0254	0.0054	0.0056	8.4	0.97	0.52	2.61
	363	0.3616	0.3937	0.0119	0.1315	—	0.0654	0.0251	0.0053	0.0055	8.9	0.97	0.46	2.61
	303	0.2656	0.3978	0.0161	0.1694	0.0107	0.0894	0.0342	0.0081	0.0087	13.3	0.93	0.35	2.62
	313	0.2781	0.4043	0.0150	0.1617	0.0099	0.0837	0.0321	0.0074	0.0078	12.7	0.96	0.36	2.61
[BMIM][Cl]:[AlCl ₃] = (1:1.2)	323	0.2670	0.4024	0.0161	0.1665	0.0107	0.0873	0.0336	0.0079	0.0084	13.2	0.94	0.35	2.60
	333	0.2848	0.4049	0.0149	0.1575	0.0093	0.0820	0.0316	0.0073	0.0076	11.9	0.95	0.37	2.59
	343	0.2785	0.4080	0.0151	0.1595	0.0100	0.0824	0.0316	0.0073	0.0076	12.6	0.96	0.35	2.61
	353	0.2698	0.4108	0.0155	0.1623	0.0101	0.0841	0.0321	0.0074	0.0078	13.1	0.95	0.34	2.62
	303	0.3483	0.2847	0.0328	0.2044	0.0156	0.0698	0.0241	0.0106	0.0096	11.3	1.11	0.42	2.90
[BMIM][Cl]:[AlCl ₃] = (1:1.3)	313	0.3722	0.2843	0.0302	0.1940	0.0142	0.0645	0.0222	0.0097	0.0087	10.4	1.11	0.44	2.90
	323	0.3719	0.2848	0.0305	0.1929	0.0143	0.0646	0.0224	0.0097	0.0088	10.3	1.11	0.44	2.88
	333	0.3809	0.2827	0.0296	0.1898	0.0136	0.0631	0.0220	0.0096	0.0087	9.8	1.11	0.45	2.87
	343	0.3639	0.2880	0.0314	0.1949	0.0147	0.0656	0.0227	0.0099	0.0089	10.5	1.11	0.43	2.89
	353	0.3762	0.2882	0.0298	0.1899	0.0139	0.0625	0.0217	0.0094	0.0084	10.2	1.11	0.43	2.88
	363	0.3760	0.2941	0.0294	0.1870	0.0137	0.0613	0.0212	0.0091	0.0082	10.2	1.11	0.42	2.88
	303	0.4330	0.2910	0.0146	0.1841	0.0053	0.0401	0.0182	0.0072	0.0065	10.9	1.10	0.32	2.20
	323	0.4469	0.2932	0.0140	0.1732	0.0050	0.0378	0.0171	0.0067	0.0061	9.9	1.11	0.33	2.21
	333	0.4706	0.2819	0.0127	0.1654	0.0048	0.0363	0.0159	0.0065	0.0058	8.9	1.12	0.37	2.28
	343	0.4635	0.2826	0.0134	0.1692	0.0049	0.0372	0.0165	0.0067	0.0060	9.2	1.12	0.36	2.25
FeCl ₃	353	0.4555	0.2875	0.0135	0.1718	0.0049	0.0374	0.0168	0.0067	0.0060	9.7	1.11	0.35	2.23
	363	0.4516	0.2845	0.0141	0.1756	0.0051	0.0385	0.0173	0.0070	0.0063	9.8	1.10	0.35	2.22
	403	0.1971	0.2161	0.0259	0.3254	0.0125	0.0916	0.0383	0.0520	0.0411	10.3	1.27	—	2.39
	423	0.2182	0.2408	0.0340	0.2890	0.0164	0.0951	0.0363	0.0392	0.0309	9.8	1.27	—	2.62

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 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 the equation

$$p_i^{\text{sat}} = m_i \cdot R \cdot T_a / (V \cdot M_i); \quad V = V_{\text{N}_2} + V_i; \quad (V_{\text{N}_2} \gg V_i) \quad (1)$$

where $R = 8.314472 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$; m_i is the mass of the transported compound; M_i is the molar mass of the compound; and V_i is its volume contribution to the gaseous phase. V_{N_2} is the volume of the carrier gas, and T_a is the temperature of the soap bubble meter. The volume of the carrier gas V_{N_2} was determined from the flow rate and the time measurement. Results from transpiration experiments are given in Table 3.

2.4. Combustion Calorimetry. An isoperibol bomb calorimeter was used for the measurement of the energy of combustion of *tert*-amylbenzene. In the present study, we used commercially available polyethylene bulbs (NeoLab, Heidelberg) of 1 cm³ volume as the sample container for liquids to reduce the capillary effect and make the encapsulation easier. The liquid specimen was transferred to the polyethen bulbs with a syringe. The narrow neck of the container was compressed with special tweezers and was sealed by heating with hot air. Then, the loaded container was placed in the bomb and burned in oxygen at a pressure of 3.04 MPa. Results from combustion experiments are given in Table 4. The detailed procedure has been described previously.¹¹ The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none

were detected. The energy equivalent of the calorimeter ϵ_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39i, N.I.S.T.). The 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.¹² The sample masses were reduced to vacuum, taking into consideration their density values (see Table S1, Supporting Information). To convert the energy of the actual bomb process to that of the isothermal process, and reducing it to standard states, the conventional procedure¹³ was applied.

3. Results and Discussion

3.1. Equilibrium Constants, Reaction Enthalpies, and Reaction Entropies. The experimental results of chemical equilibria study of systems I and II are listed in Tables 1 and 2. The experimental values of K_x for all reactions measured in this work are only slightly changed with the temperature. According to our earlier results^{2,14,15} for the reactions R1–R4 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. Hence, reaction enthalpy, $\Delta_r H_m^\circ$, can be easily calculated from the temperature dependence of the ratios K_x (see Table 5). Experimental values of K_x for reactions R1–R4 were approximated as a function of temperature by the linear equation $\ln K_x = a + b \cdot (T/K)^{-1}$ 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 results are presented in Table 5. The errors in the thermodynamic functions from equilibrium study are given by the standard deviations for the meaningful level 0.05.

TABLE 3: Vapor Pressures p and $\Delta_f H_m^\circ$ of *tert*-amyl 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	$(p_{exp} - p_{calc})/Pa$	$\Delta_f H_m/kJ \cdot mol^{-1}$
$\Delta_f H_m(298 K) = (52.30 \pm 0.31) kJ \cdot mol^{-1}$						
$\ln(p/Pa) = 283.56/R - 72941.04/(R \cdot (T/K)) - 69.24/R \ln((T/K)/298.15)$						
274.5	2.00	2.11	4.21	16.60	-0.3	53.94
277.4	2.18	1.76	4.23	21.32	-0.4	53.74
280.6	2.34	1.43	4.29	28.00	-0.3	53.52
283.5	2.28	1.07	4.29	36.19	0.5	53.31
286.6	2.86	1.07	4.29	45.28	-0.3	53.10
289.5	1.75	0.521	1.04	57.17	0.2	52.90
292.4	1.90	0.442	1.04	72.82	2.0	52.70
293.4	1.19	0.251	1.00	80.24	3.9	52.63
296.5	1.95	0.347	1.04	95.05	-0.5	52.41
298.3	1.75	0.268	1.00	110.02	1.4	52.29
301.4	2.06	0.261	1.04	133.80	-1.1	52.08
303.4	2.31	0.251	1.00	154.36	-0.3	51.94
306.4	2.91	0.261	1.04	188.39	-0.7	51.73
308.2	3.20	0.251	1.00	213.82	0.9	51.60
311.3	3.72	0.248	0.99	252.24	-7.9	51.39
313.5	5.36	0.301	1.00	298.01	-0.9	51.24
316.3	5.24	0.248	0.99	354.43	-1.3	51.04
318.3	5.94	0.248	0.99	401.38	-0.4	50.91

^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 $T = 243 K$.

TABLE 4: Results for Typical Combustion Experiments at $T = 298.15 K$ ($p^\circ = 0.1 MPa$) of the *tert*-Amylbenzene^a

$m(\text{substance})/g^b$	0.344025	0.255835	0.220882	0.249176	0.226063	0.207593
$m'(\text{cotton})/g^b$	0.000945	0.000924	0.000865	0.001196	0.000939	0.001024
$m''(\text{polythen})/g^b$	0.295058	0.290247	0.342249	0.323979	0.344822	0.3345
$\Delta T_c/K^c$	1.94682	1.6701	1.72936	1.75336	1.75237	1.66539
$(\epsilon_{calor}) \cdot (-\Delta T_c)/J$	-28829	-24731.2	-25608.7	-25964.1	-25949.5	-24661.4
$(\epsilon_{cont}) \cdot (-\Delta T_c)/J$	-36.23	-30.46	-31.69	-32.41	-32.17	-30.36
$\Delta U_{decomp} HNO_3/J$	51.36	44.2	45.39	0.00	45.99	44.5
$\Delta U_{corr}/J^d$	9.4	7.76	8.0	8.38	8.13	7.64
$-m' \cdot \Delta_c u''/J$	16.01	15.66	14.66	20.27	15.91	17.35
$-m'' \cdot \Delta_c u''/J$	13677.27	13454.25	15864.78	15017.88	15984.05	15505.58
$\Delta_c u^\circ(\text{liq})/(J \cdot g^{-1})$	-43924.6	-43933.7	-43949.2	-43944.8	-43915.1	-43916.0
			-43930.6 \pm 5.9			

^a For the definition of the symbols, see ref 13. Macrocalorimeter: $T_h = 298.15 K$; $V(\text{bomb}) = 0.320 dm^3$; $p^i(\text{gas}) = 3.04 MPa$; $m^i(H_2O) = 1.00 g$. ^b Masses obtained from apparent masses. ^c $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\epsilon_{cont}) \cdot (-\Delta T_c) = (\epsilon^i_{cont}) \cdot (T^i - 298.15 K) + (\epsilon^f_{cont}) \cdot (298.15 K - T^f + \Delta T_{corr})$. ^d ΔU_{corr} , the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in ref 13.

3.2. Vapor Pressure and Vaporization Enthalpy of *tert*-Amylbenzenes. Experimental vapor pressures of the *tert*-amylbenzenes measured in this work were treated with eqs 2 and 3, respectively

$$R \cdot \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_f^\circ C_p \cdot \ln\left(\frac{T}{T_0}\right) \quad (2)$$

$$\Delta_f^\circ H_m(T) = -b + \Delta_f^\circ C_p \cdot T \quad (3)$$

where p_i^{sat} is vapor pressure; a and b are adjustable parameters (Table 3); T_0 is an arbitrarily chosen reference temperature (T_0 is 298.15 K in this work); and $\Delta_f^\circ C_p$ is the difference of the molar heat capacities of the gaseous and the liquid phase. Values of $\Delta_f^\circ C_p$ were calculated from isobaric molar heat capacity C_p° of *tert*-amyl-substituted benzene using the group contribution method of Chickos and Acree.¹⁶ To assess the uncertainty of the vaporization enthalpy, the experimental data were approximated with the linear equation $\ln(p_i^{\text{sat}}) = f(T^{-1})$ using the method of least-squares. The uncertainty in the enthalpy of vaporization was assumed to be identical with the average deviation of experimental $\ln(p_i^{\text{sat}})$ values from this linear correlation (uncertainties in values of $\Delta_f^\circ C_p$ are not taken into

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

reaction	$\langle T \rangle^a$	a	b	$\Delta_r H_m^\circ{}^b$	$\Delta_r S_m^\circ{}^b$
	K			$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$
R1	354.5	2.1	77.6	-0.7 ± 0.6	17.4 ± 1.9
R2	354.5	0.57	-149.4	1.2 ± 0.5	4.7 ± 1.4
R3	354.5	-1.2	100.8	-0.8 ± 1.0	-9.8 ± 3.2
R4	354.5	0.86	29.3	-0.2 ± 0.5	7.2 ± 1.5

^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 R1 to R4 were derived for the average temperatures given in column 2. It was assumed that the enthalpies of the reaction hardly change on passing from the average temperature of the experimental range to $T = 298 K$.

account). This experimental and calculation procedure has been validated with measurements of vapor pressures of *n*-alkanols.⁹ Vapor pressures derived from the transpiration method were reliable to 1–3%.

3.3. Energy of Combustion and Enthalpy of Formation of *tert*-Amylbenzene. Results of combustion experiments on *tert*-amylbenzene are given in Table 4. The value of the standard specific energy of combustion $\Delta_c U^\circ = -(43930.6 \pm 5.9) J \cdot g^{-1}$ has been used to derive the standard molar enthalpy of

combustion $\Delta_c H_m^\circ = -(6522.4 \pm 2.3) \text{ kJ} \cdot \text{mol}^{-1}$ and the standard molar enthalpy of formation in the liquid state $\Delta_f H_m^\circ(\text{liq}) = -(92.9 \pm 2.7) \text{ kJ} \cdot \text{mol}^{-1}$ based on the reaction



$\Delta_f H_m^\circ(\text{liq})$ of the *tert*-amylbenzene has been obtained from the enthalpic balance according to eq 5

$$\Delta_f H_m^\circ(\text{liq}, \text{C}_{11}\text{H}_{16}) = 11 \times \Delta_f H_m^\circ(\text{g}, \text{CO}_2) + 8 \times \Delta_f H_m^\circ(\text{liq}, \text{H}_2\text{O}) - \Delta_c H_m^\circ \quad (5)$$

where molar enthalpies of formation of $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$ were taken from the literature, as recommended by CODATA.¹² The total uncertainty of $\Delta_f H_m^\circ(\text{liq})$ was calculated according to the guidelines presented by Olofsson.¹⁷ The uncertainty assigned to $\Delta_f H_m^\circ(\text{liq})$ 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 .

The enthalpy of formation in the gaseous phase of any compound is made up of two contributions according to equation: $\Delta_f H_m^\circ(\text{g}) = \Delta_f^\circ H_m + \Delta_f H_m^\circ(\text{l})$, where $\Delta_f^\circ H_m$ is the enthalpy of vaporization and $\Delta_f H_m^\circ(\text{l})$ is the enthalpy of formation in the liquid state. The vaporization enthalpy of *tert*-amylbenzene derived in this work (Table 3) has been used in conjunction with the results from combustion experiments (Table 4) for further calculation of the gaseous standard enthalpies of formation, $\Delta_f H_m^\circ(\text{g}) = -(40.6 \pm 2.7) \text{ kJ} \cdot \text{mol}^{-1}$ at 298 K.

4. Quantum Chemical Calculations

4.1. Methods of Calculations. Standard ab initio molecular orbital calculations were performed with the Gaussian 03 Rev. 04 series of programs.¹⁸ 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 R1–R4. The B3LYP/6-31G(d,p) method was used for the calculation of the geometry parameter, ZPE values, and normal-mode frequencies. The enthalpy values at $T = 298 \text{ K}$ were evaluated according to standard thermodynamic procedures.¹⁹

4.2. Validation of Enthalpy of Formation of *tert*-Amylbenzene Using G3MP2 Calculations. In the present work, enthalpy of formation $\Delta_f H_m^\circ(\text{g}, 298 \text{ K})$ of *tert*-amylbenzene has been calculated on the basis of the eight selected isodesmic and homodesmic reactions presented in Table 6. Using enthalpies of reactions calculated by G3MP2 together with available²⁰ experimental enthalpies of formation, $\Delta_f H_m^\circ(\text{g}, 298 \text{ K})$, for other reaction participants, theoretical enthalpies of formation of *tert*-amylbenzene have been calculated (see Table 6). Results calculated from isodesmic and homodesmic reactions are in close agreement, and the average value from all eight reactions $\Delta_f H_m^\circ(\text{g}, 298 \text{ K})_{(\text{tert-amylbenzene})} = -(38.5 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}$ has been calculated. Having established this theoretical value, the enthalpy of formation of the liquid *tert*-amylbenzene could be estimated by the following equation

$$\Delta_f H_m^\circ(\text{liq})_{\text{G3MP2}} = \Delta_f H_m^\circ(\text{g})_{\text{G3MP2}} - \Delta_f^\circ H_m \quad (6)$$

The enthalpy of vaporization, $\Delta_f^\circ H_m(298 \text{ K}) = (52.3 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$, of *tert*-amylbenzene has been measured in this work (see Table 3). Thus, using eq 6 the enthalpy of formation of

TABLE 6: Results from G3MP2 Calculations of $\Delta_f H_m^\circ(\text{g})$ for *tert*-Amylbenzene at 298 K in $\text{kJ} \cdot \text{mol}^{-1}$

reaction	G3MP2
<i>tert</i> -amylbenzene + $5\text{CH}_4 = 3\text{C}_2\text{H}_4 + 3\text{CH}_3=\text{CH}-\text{CH}=\text{CH}_3 + 5\text{C}_2\text{H}_6$	−42.8
<i>tert</i> -amylbenzene + $4\text{CH}_4 = \text{toluene} + 4\text{C}_2\text{H}_6$	−39.3
<i>tert</i> -amylbenzene + $\text{CH}_4 = \text{ethyl-benzene} + 2\text{-methyl-propane}$	−38.1
<i>tert</i> -amylbenzene + ethyl-benzene = iso-propyl-benzene + iso-butylbenzene	−35.3
<i>tert</i> -amylbenzene + $\text{C}_3\text{H}_8 = \text{iso-butylbenzene} + 2\text{-methyl-propane}$	−38.1
<i>tert</i> -amylbenzene = 1-methyl-3- <i>tert</i> -butylbenzene	−39.5
<i>tert</i> -amylbenzene = 1-methyl-4- <i>tert</i> -butylbenzene	−38.6
<i>tert</i> -amylbenzene + $7\text{CH}_4 = \text{C}_2\text{H}_2 + 3\text{C}_2\text{H}_4 + 5\text{C}_3\text{H}_8$	−35.9
average	−38.5 ± 1.6^a

^a Experimental value: $\Delta_f H_m^\circ(\text{g}) = -(40.6 \pm 2.7) \text{ kJ} \cdot \text{mol}^{-1}$.

TABLE 7: Results of Calculations of the Enthalpies of Reaction, $\Delta_r H_m^\circ$ ($\text{kJ} \cdot \text{mol}^{-1}$), Entropies of Reaction $\Delta_r S_m^\circ$ ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), and Gibbs Energies of Reaction, $\Delta_r G_m^\circ$ ($\text{kJ} \cdot \text{mol}^{-1}$), in the Gaseous Phase at 298 K

reaction	G3MP2			DFT		
	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
R1	—	—	—	−1.60	−0.70	3.02
R2	—	—	—	4.45	1.39	−10.26
R3	1.49	−0.05	−5.17	0.37	0.14	−0.77
R4	−0.36	−0.32	0.13	0.74	0.31	−1.44

TABLE 8: Enthalpies of Reactions 1–4, $\Delta_r H_m^\circ$, in the Gaseous and the Liquid Phase at $T = 298 \text{ K}$ in $\text{kJ} \cdot \text{mol}^{-1}$

reaction	$\Delta_r H_m^\circ(\text{g})$	$\Delta_r H_m^\circ(\text{g})$	$\Delta_r H_m^\circ(\text{liq})$	$\Delta_r H_m^\circ(\text{liq})$	$\Delta_r H_m^\circ(\text{liq})$
	(DFT)	(G3MP2)	(DFT)	(G3MP2)	(exp)
R1	−0.70	—	−2.4	—	−0.7 ± 0.6
R2	1.39	—	3.1	—	1.2 ± 0.5
R3	0.14	−0.05	0.6	0.5	−0.8 ± 1.0
R4	0.31	−0.32	1.2	0.6	−0.2 ± 0.5

tert-amylbenzene, $\Delta_f H_m^\circ(\text{liq})_{\text{G3MP2}} = -(90.8 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}$, was calculated, and this value is in excellent agreement with our combustion result $\Delta_f H_m^\circ(\text{liq})_{\text{exp}} = -(92.9 \pm 2.7) \text{ kJ} \cdot \text{mol}^{-1}$. Such good agreement between experimental and theoretical G3MP2 values is a valuable check of their mutual consistency.

4.3. Thermodynamic Functions of Reactions R1 to R4. It is well established that chemical reactions of isomerization and transalkylation such as those in reactions R1–R4 are thermodynamically favorable. Thus, desired yields of goal products could be possibly predicted with the help of ab initio calculations. In our recent work,^{2,21–23} the remarkable ability of the G3MP2 ab initio method to accurately predict gaseous enthalpies of formation of organic compounds was demonstrated. To validate this procedure for *tert*-amylbenzenes, the thermodynamic functions, Gibbs energy, $\Delta_r G_m^\circ$, reaction enthalpy, $\Delta_r H_m^\circ$, and reaction entropy, $\Delta_r S_m^\circ$, were calculated for the gas phase reactions R1–R4 using the B3LYP and G3MP2 methods. Calculated values are given in Table 7.

4.4. Comparison of Reaction Enthalpies Obtained from Equilibrium Studies and from Ab Initio Calculations. Generally, the enthalpy of chemical reaction, $\Delta_r H_m^\circ$, 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 R1–R4 obtained from experimental studies and from

TABLE 9: Thermochemical Results for Alkylbenzenes at $T = 298$ K ($p^\circ = 0.1$ MPa) in $\text{kJ}\cdot\text{mol}^{-1}$

	$\Delta_f H_m^\circ(\text{liq})$	$\Delta_f^\circ H_m^b$	$\Delta_f H_m^\circ(\text{g})(\text{exp.})$	$\Delta_f H_m^\circ(\text{g})(\text{calc.})^a$	H_S^b
<i>tert</i> -butylbenzene	-71.2 ± 0.5^c	47.5 ± 0.4^c	-23.7 ± 0.7	-35.3	11.6
<i>tert</i> -amylbenzene	-92.9 ± 2.7	52.3 ± 0.3	-40.6 ± 2.7	-56.8	16.2

^a Calculated as the sum of strain-free increments (see text). ^b Strain enthalpy $H_S = \Delta_f H_m^\circ(\text{g})(\text{exp.}) - \Delta_f H_m^\circ(\text{g})(\text{calc.})$. ^c Data from ref 2.

ab initio calculations. Using the DFT and G3MP2 procedure, the standard reaction enthalpies, $\Delta_r H_m^\circ(\text{g})$, of the reactions R1–R4 in the ideal gaseous phase at 298 K were calculated (see Tables 7 and 8). The values of $\Delta_r H_m^\circ(\text{g})$ are related to the standard reaction enthalpies, $\Delta_r H_m^\circ(\text{liq})$, in the liquid state by

$$\Delta_r H_m^\circ(\text{liq}) = \Delta_r H_m^\circ(\text{g}) - \sum_i \nu_i \Delta_i^\circ H_{mi} \quad (7)$$

where $\Delta_i^\circ H_{mi}$ 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 R1–R4 are available (see Table S2 in Supporting Information). Enthalpies of reaction $\Delta_r H_m^\circ(\text{g})_{\text{DFT}}$ and $\Delta_r H_m^\circ(\text{g})_{\text{G3MP2}}$ calculated directly from enthalpies of reaction participants using B3LYP and G3MP2 are given in Tables 7 and 8. Enthalpies of reactions R1–R4, $\Delta_r H_m^\circ(\text{liq})_{\text{DFT}}$ and $\Delta_r H_m^\circ(\text{liq})_{\text{G3MP2}}$, in the liquid phase calculated according to eq 7 are listed for comparison with experimental values in Table 8. The calculated values of the $\Delta_r H_m^\circ(\text{liq})_{\text{DFT}}$ and $\Delta_r H_m^\circ(\text{liq})_{\text{G3MP2}}$ for reactions R1–R4 are in good agreement (within the boundaries of experimental uncertainties) with those derived from the chemical equilibrium studies. It should be stressed that the values of the $\Delta_r H_m^\circ(\text{liq})_{\text{DFT}}$ and $\Delta_r H_m^\circ(\text{liq})_{\text{G3MP2}}$ for reactions R1–R4 were calculated using enthalpies H_{298} (see Table S3, Supporting Information) of the reaction participants directly available from the ab initio protocol. In this case, it has been possible to avoid any ambiguity due to calculations leading to the enthalpies of formation, $\Delta_f H_m^\circ(\text{g})$, using isodesmic or homodesmic reactions (see Table 6) as described above in section 4.2. Thus, the DFT and the G3MP2 methods could be successfully applied to the calculation of reaction enthalpies for reactions similar to R1–R4.

The composite G3MP2 method used in this work to predict enthalpies of formations of *tert*-amylbenzene and parent molecules is quite time-consuming. Small molecules such as toluene only required a CPU time of 22 min for the longest step 4 with QCISD(T)/6-31G(d). For slightly larger molecules, such as *tert*-amylbenzene, the required job CPU time was already 14 h (the calculations were performed at University Computational Centre with help of Linux Cluster AMD Opteron 252 using two processors and 2500 Mb RAM). For di-*tert*-amylbenzenes, it was not possible to complete our calculations within two weeks even using the resources of the University Computational Centre.

4.5. Strain of *tert*-Amylbenzene in Comparison to *tert*-Butylbenzene. The relationship between the structure of organic compounds and their energetics is one of the fundamental problems of contemporary thermochemistry. The quantitative evaluation of substituent effects in terms of $\Delta_f H_m^\circ(\text{g})$ is one of the possible approaches to the general problem of elucidating how the individual parts of a molecule influence each other. We have been tempted to invoke an idea of “Spannungsenergie”, introduced by von Bayer²⁴ to account for structure–energy relationships. The concept of “strain energy”, H_S , in organic molecules although not unambiguously defined is conceptually useful, because in the value of H_S the sum of the overall interactions in a molecule is collected.²⁵

We define the strain of a molecule¹⁵ as the difference between the experimental standard enthalpy of formation $\Delta_f H_m^\circ(\text{g})$ and the calculated sum of the strain-free increments using the Benson method.²⁶ The system of strain-free increments is based on the standard enthalpies of formation $\Delta_f H_m^\circ(\text{g})$ of simple homologous (“strainless”) molecules. Strain-free group additivity increments for hydrocarbons²⁷ and arenes²⁸ are well-defined. Their advantage with respect to the classic Benson increments²⁶ is the possibility to determine strain enthalpies. All the increments necessary in this work are as follows:^{27,28} $\text{CH}_3[\text{C}] = -42.05 \text{ kJ}\cdot\text{mol}^{-1}$; $\text{CH}_2[2\text{C}] = -21.46 \text{ kJ}\cdot\text{mol}^{-1}$; $\text{CH}[3\text{C}] = -9.04 \text{ kJ}\cdot\text{mol}^{-1}$; $\text{C}[4\text{C}] = -1.26 \text{ kJ}\cdot\text{mol}^{-1}$; $\text{C}_\text{B}\text{H}[2\text{C}_\text{B}] = 13.72 \text{ kJ}\cdot\text{mol}^{-1}$; $\text{C}_\text{B} [\text{C}, 2\text{C}_\text{B}] = 23.51 \text{ kJ}\cdot\text{mol}^{-1}$ (C_B represents the aromatic C atoms). Using these group-additivity parameters and the values of $\Delta_f H_m^\circ(\text{g})$ of alkylbenzenes (Table 9), the values of strain enthalpies $H_S = \{\Delta_f H_m^\circ(\text{g}) - \Sigma \text{ increments}\}$ of *tert*-butylbenzene and *tert*-amylbenzene have been estimated (Table 9). The strain of $H_S = 11.6 \text{ kJ}\cdot\text{mol}^{-1}$ for the *tert*-butylbenzene describes the intrinsic strain of the molecule due to steric repulsions of methyl groups and the benzene ring attached to the quaternary carbon atom. The strain of $H_S = 16.2 \text{ kJ}\cdot\text{mol}^{-1}$ for the *tert*-amylbenzene indicates that in this molecule an additional steric repulsion between the alkyl group with the benzene ring should be taken into account. These strain effects have to be considered in any additive scheme as non-nearest-neighbor interactions which are specific for the branched alkylbenzenes.

Conclusions

The object of this research was to obtain the milder catalysts of *tert*-amylation of benzene and toluene to prevent rearrangements of the alkyl substituent during the investigation. None of the catalysts (chloroaluminate ionic liquids, FeCl_3 , ion-exchange resin Amberlyst 21) used in this study were able to avoid the isomerization of the *tert*-amyl substituent completely. However, in contrast to the traditional Friedel–Crafts catalysts (AlCl_3 or AlBr_3), mild catalysts applied in this work have allowed us to determine thermodynamic characteristics of the isomerization and transalkylation of *tert*-amylbenzenes and *tert*-amyltoluenes in the systems I and II (see Figure 1).

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Supporting Information Available: Auxiliary data for the combustion experiments (Table S1); enthalpies of vaporization of alkylbenzenes (Table S2); and total energies at 0 K and enthalpies at 298 K (in Hartree) of the molecules studied in this work (Table S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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