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Thermochemistry of ionic liquid-catalysed reactions. Isomerisation and transalkylation of *tert*-alkyl-benzenes. Are these systems ideal?

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ABSTRACT

The chemical equilibrium of mutual interconversions of *tert*-alkyl-benzenes was studied in the temperature range (286 to 423) K using chloroaluminate ionic liquids as a catalyst. The knowledge of the activity coefficients is required in order to obtain the thermodynamic equilibrium constants K_a. A well established procedure, COSMO-RS, has been used to assess activity coefficients of the reaction participants in the liquid phase. Enthalpies of five reactions of isomerisation and transalkylation of *tert*-alkyl-benzenes were obtained from temperature dependences of the corresponding equilibrium constants in the liquid phase. For the sake of comparison, high-level *ab initio* calculations of the reaction participants have been performed using the Gaussian-03 program package. Absolute electronic energy values of the molecules have been obtained using B3LYP and G3MP2 level. Using these results enthalpies of reaction of isomerisation and transalkylation of *tert*-alkyl-benzenes in the liquid phase based on the first principles are found to be in good agreement with the data obtained from the thermochemical measurements.

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1. Introduction

The Friedel–Crafts alkylation of benzene with long chain α-olefins is used industrially for the manufacture of more than two million tons per annum of linear alkylbenzenes worldwide [1]. Recently, a few of examples of the Friedel–Crafts alkylations of aromatic compounds with alkenes have been reported to proceeded in ionic liquids (ILs), a kind of novel and promising solvents for synthetic chemistry [2,3]. An advantage of the chloroaluminate ILs in comparison to conventional catalysts ($AlCl_3$ or $AlBr_3$, or hazardous Brønsted acids such as HF) 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 [4,5]. 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.

In our recent studies [4,5] of chemical interconversions of *tert*-alkyl substituted benzenes (see figure 1) using chloroaluminate ionic liquids as catalysts we established very mild and selective conditions for investigation of chemical equilibria in such systems. This work extends our previous studies [4,5] of chemical equilibrium of *tert*-alkyl substituted benzenes using chloroaluminate ionic liquids as the catalyst with the two new separate model systems IV and V (see figure 1).

Systematic studies of the temperature dependences of equilibrium constants of the reactions (1) to (7) provide a knowledge of their thermodynamic functions (reaction enthalpies, $\Delta_r H^\circ_m$, and reaction entropies, $\Delta_r S^\circ_m$) according to the *The Second Law Method* [4].

For a general chemical reaction in the liquid phase, *e.g.*,

$$A + B \rightleftharpoons C + D, \tag{9}$$

the true thermodynamic equilibrium constant, K_a, is defined as the ratio of the activities a_i of the products and the reagents under equilibrium conditions. Taking into account that $a_i = \gamma_i \cdot x_i$, the true thermodynamic constant K_a of the reaction (9) is expressed:

$$K_a = \frac{a_C \cdot a_D}{a_A \cdot a_B} \cdot = \frac{\gamma_C \cdot \gamma_D}{\gamma_A \cdot \gamma_B} \cdot \frac{x_C \cdot x_D}{x_A \cdot x_B} = K_\gamma \cdot \frac{x_C \cdot x_D}{x_A \cdot x_B}, \tag{10}$$

where γ_i is the activity coefficient of component i, and K_γ is their ratio. From the van't Hoff relation

$$\mathrm{d}\ln K_a/\mathrm{d}T = \Delta_r H^\circ_m/RT^2, \tag{11}$$

the slope of a plot $R(\ln K)$ *vs.* $1/T$ gives the standard enthalpy of reaction $\Delta_r H^\circ_m$ if the temperature dependence of the equilibrium constant K_a is measured. From the enthalpy of reaction (9), the enthalpy of formation of a particular reaction participant can be determined provided that the values of $\Delta_f H^\circ_m$ for other species are known. This procedure, involving study of the changes of

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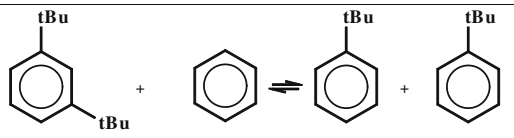
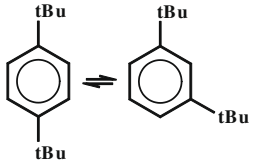
System I



[1]

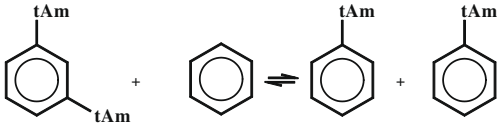
m-di-tBuB + Benzene = tBuB + tBuB



[2]

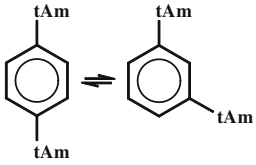
p-di-tBuB = m-di-tBuB

System II



[3]

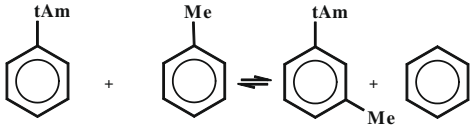
m-di-tAmB + Benzene = tAmB + tAmB



[4]

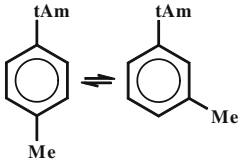
p-di-tAmB = m-di-tAmB

System III



[5]

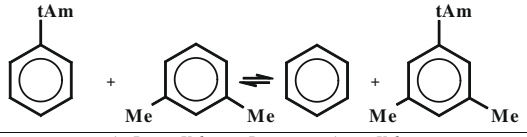
tAmB + Toluene = m-tAmT + Benzene



[6]

p-tAmT = m-tAmT

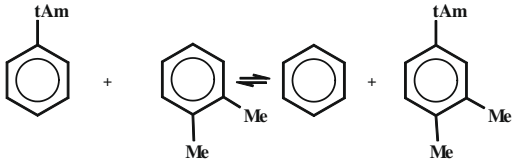
System IV



[7]

tAmB + m-Xylene = Benzene + tAm-m-Xylene

System V



[8]

tAmB + o-Xylene = Benzene + tAm-o-Xylene

FIGURE 1. Five systems of transalkylation and isomerisation reactions of *tert*-alkyl substituted benzenes studied (acronym *tBu* is used for the alkyl substituent $(CH_3)_3C–$ and acronym *tAm* is used for the alkyl substituent $CH_3–CH_2–(CH_3)_2C–$).

equilibrium constants with temperature, is referred to as *Second Law Method*.

As a rule, values of γ_i depend on the mixture composition and should be calculated by any of available methods, *e.g.* COSMO-RS

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