

## DFT study on the mechanism of alkylation reaction between isobutane and 2-butene catalyzed by chloroaluminate ILs

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The mechanism of C4 alkylation reactions catalyzed by chloroaluminate ILs is studied by quantum chemical methods, with the Gaussian 03w using DFT B3LYP method, at 6-31G\* basis set level. It is found that  $Al_2Cl_7^-$  is the catalytically active component, and  $AlCl_3$  is the final catalytically active center in the Lewis acid. 2,2,3-TMP from the reaction between tert-butyl cation and 2-butene is the product controlled by kinetics, while 2,2,4-TMP is the product controlled by thermodynamics with greater yield. And the main reaction mechanism between isobutane and 2-butene catalyzed by ionic liquid  $Et_2NH-Al_2Cl_7$  is as follows:

**I. Chain initiation:** the  $\pi$ -electrons of 2-butene and  $AlCl_3$  can form a stable ADC complex catalyzed by ionic liquid  $[(C_2H_5)_2NH][Al_2Cl_7]$ .  $Al_2Cl_7^-$ ,  $AlCl_4^-$  and cations are combined to form the neutral organic salts. The formation of ADC complex is a spontaneous process.

**II. Chain propagation:** the ADC complex can act with isobutane to extract hydrogen and form tert-butyl cation. The activation energy of the reaction is 54.26kJ/mol, which means the reaction can easily occur. The tert-butyl cation acts with the double bond of 2-butene, forming a three-membered ring carbon onium ion which can rearrange to form 2,2,3-TMP<sup>+</sup>; while the 2,2,3-TMP<sup>+</sup>, through a methyl shift, rearranges to generate 2,2,4-TMP<sup>+</sup> which is relatively more stable with a low energy.

**III. Chain termination:** 2,2,4-TMP<sup>+</sup> captures another H- from isobutane to form 2,2,4-TMP and tert-butyl cation, termination the chain termination reaction.

**IV. Circular reaction:** The above product tert-butyl cation acts with 2-butene to generate another 2,2,3-TMP<sup>+</sup>. After rearrangement it can act with isobutane and circular reaction continues until the reaction completes. The results can explain the experimental phenomena very well.

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