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 AlCl− is the catalytically active component, and AlCl3 is the final catalytically active center in the Lewis acid. 2,2,3-TMP from the reaction between tert-butyl action 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 Et2NH-AlCl7 is as follows:

I. Chain initiation: the -electrons of 2-butene and AlCl3 can form a stable ADC complex catalyzed by ionic liquid [(C6H5)3NH] Al2Cl7. AlCl4− 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 is means the reaction can easily occur. The tert-butyl cation acts with the double bond of 2-butene, forming a three-membered ring carbononium ion which can rearrange to form 2,2,3-TMP+; while the 2,2,3-TMP+, through a methyl shift, rearranges to generate 2,2,4-TMP+ which is relatively more stable with a low energy.

III. Chain termination: 2,2,4-TMP+ 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+. 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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