Mechanistic Study of the Conversion of Primary Alcohols and Butadiene to Branched Ketones Using Rhodium Catalyst

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The direct formation of ketones without premetalation is a key priority in catalysis research as it offers more straightforward reaction process and fewer steps [1]. Here we present our investigation of the mechanism for the conversion 3-methoxybenzyl alcohol and butadiene into branched isobutyl ketone with rhodium (I) complex catalyst under basic condition using density functional theory [2]. The reaction consists of four main steps: (I) oxidation of the alcohol reactant to generating the corresponding aldehyde and rhodium(I) hydride complex as active catalyst, (ii) hydrogenation of butadiene to form the allyl–Rh(I) complex, (iii) carbonyl addition from the allylic carbon to produce rhodium(I) alkoxide intermediate, and (iv) hydrogen transfer processes to generate the desired ketone product, which is released in its enolate form. The rate-determining states are in the carbonyl addition process (both intermediate and transition state) with an energy barrier of +30.4 kcal/mol. The formation of the linear ketone is hindered by steric effects from two PPh₃ ligands bound to the Rh center throughout the reaction. Moreover, the positions of transferred hydrogens in our proposed catalytic cycle are consistent with the results of the deuterium labeling experiment, highlighting the hydrogen (auto)transfer process in this conversion of primary alcohol to branched ketones.

References:

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