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DFT calculations of the alkylation reaction mechanisms of isobutane and 2-butene catalyzed by Brönsted acids

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Abstract

Density functional theory method was employed to determine the alkylation reaction course of 2-butene and isobutane. A carbonium ion mechanism is supported through this theoretical simulation. The first step is the formation of *sec*-$C_4H_9^+$ from the protonation of 2-butene. The carbonium ion reacts with isobutane to form *tert*-butyl carbonium ion via hydride transfer. This carbonium ion reacts with 2-butene quickly to produce trimethylpentane carbonium ion (TMP^+), which is finally converted to TMP at a high reaction rate via hydride transfer from isobutane. Their transition states are obtained by QST2 method and the transition states are verified by frequency analysis. The calculation results indicate that the energy barrier of each reaction is below zero, suggesting that each reaction step is fast because of the characteristics of carbonium ions. However, the additive reaction is considered to be the rate-limiting step.

Keywords: Alkylation; Addition reaction; Hydride transfer; Molecular simulation

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1. Introduction

High octane number gasoline components, such as 2,2,3-trimethylpentane (TMP), can be obtained by reacting isobutane with butene catalyzed by concentrated H_2SO_4, HF or other strong acids. Nowadays, it becomes even more important to study this reaction both experimentally and theoretically because the increasing demands for cleaner gasoline.

Several investigations on the reaction mechanisms have been carried out [1–5]. Neurock and co-workers [4] used density functional theory (DFT) methods to examine the mechanisms of hydride transfer and alkylation catalyzed by phosphotungstic acid. DFT calculations suggest that hydride transfer from isobutane to an adsorbed alkyl intermediate on the surface of phosphotungstic acid proceeds via formation of a surface carbonium ion transition state (TS). Subsequent complexation of the carbonium ion with isobutane forms a shared-hydride intermediate. Thus, the overall barrier to hydride transfer is the energy required to convert the adsorbed alkyl species to a carbonium ion. Formation of the carbonium ion from alkoxide or π-bound adsorbed states is not affected by the presence of isobutane. Hydride transfer to a tertiary carbon atom occurs with a substantially lower barrier than transfer to a secondary carbon atom, because of the greater stability of the more substituted carbonium. Alkylation of an adsorbed alkyl species also proceeds through a carbonium ion transition state. The transition state for alkylation is stabilized by interaction with the alkylating alkene.

Hommeltoft and co-workers [5] carried out simulations with models that are more consistent with the general practice of the refinery applications. They demonstrate that as the TMP concentration increases, the rate of degradation of TMP and the formation of ASO also increases. This is why the product concentration was kept low in the isobutane alkylation reactors. It also explains partially the beneficial effect of the multifold excess of isobutane used in the industrial isobutane alkylation with olefins. Their model also shows that isobutane has an inhibiting effect on the isooctane decomposition.

C4 alkylation reactions follow similar rules in both homogeneous and heterogeneous systems. Ionic liquid catalysts have shown high activity in the production of isooctane under the batch conditions [3]. It has been found that a higher molar ratio of isobutane (iC4/C4 = more than 10) results in better activity. At temperatures around 343–353 K, a maximum

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in isooctane selectivity is observed. Using a step-up design under batch conditions with a dilute mixture of isobutane and alkene, the reactions catalyzed by a variety of ionic liquids were found to follow a pattern based on acid strength of the catalysts.

The isobutane and butene reaction is complex because, in addition to the main reactions, many other reactions such as olefin polymerization and cracking also take place. Nevertheless, the reaction is believed to proceed via a carbonium ion mechanism [6–13]. First, rapid protonation of 2-butene to *sec*-butyl carbonium ion followed by the hydride transfer between isobutane and *sec*-butyl carbonium ion forms *tert*-butyl carbonium ion and *n*-butane. The resulting *tert*-butyl carbonium ions react rapidly with 2-butene to produce TMP^+, which is converted to 2,2,3-TMP via hydride transfer from isobutane. A new *tert*-butyl carbonium ion is generated and during the hydride transfers process and another reaction cycle starts. Of course, there are numerous ways the cycle could be terminated, such as alkene formation via dehydrogenation. However, the proposed mechanism above is very difficult to verify experimentally, because it is almost impossible to detect the intermediates due to the rigorous reaction conditions and the complexity of the reaction system. Furthermore, experimental measurements of reaction equilibrium for these steps are not available. The aim of this paper is to investigate the mechanism of the reaction between isobutane and butene catalyzed by Brönsted acids through theoretical calculations using DFT methods of quantum chemistry. A better understanding of the chemistry of C4 alkylation reaction will help the selection of acid catalysts and will improve the reaction conditions to achieve better yields.

2. Calculation models and methods

Because high activity reactants like H^+ (from Brönsted acids) and 2-butene are involved in the initiation step, we omitted this uncontrollable step and just focussed on the reaction between protonated butene and isobutane. Model 1-1 in Fig. 1 shows the hydride transfer reaction and the formation of *tert*-butyl carbonium ion. Model 1-2 in Fig. 1 shows the addition reaction of *tert*-butyl carbonium ion and butene. The distance between H14 and C15 atoms (R_{H14C15}) is defined as the reaction coordinate for Model 1-1 and the total energy is scanned as the length of R_{H14C15} deceases until H14 shifts to C15. For Model 1-2, R_{C1C13} is defined as the reaction coordinate and the two carbon atoms are attracted to form a bond. Both of the Models are calculated by full optimization using SCAN method first and then using QST2 method to look for transition states. The two methods supplement each other and frequency analysis is done to confirm the transition states. Anions of Brönsted acids are ignored in order to save computational time and resources. The outstanding calculational method of B3LYP at 6-31+G* level is used by Gaussian 03W programme [14–21].

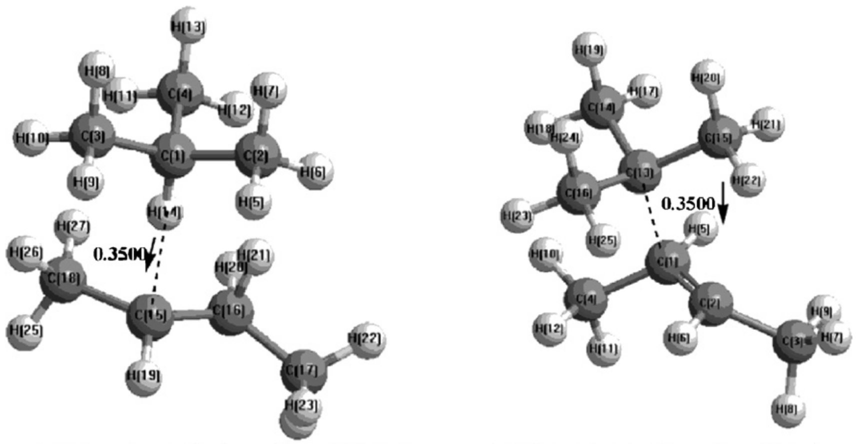
3. Results and discussion

3.1. Mechanism of the reaction between protonated butene and isobutane

At first, we carried out full geometry optimization for 2-butene and isobutane. The isobutane molecular geometry and charge density are obtained, which are identical to experimental results (Fig. 2). Its energy is −158.4641 a.u. (equal to −416031.61 kJ/mol); its dipole moment is 0.1315 Debye; and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy are −0.32365 and 0.00849 a.u., respectively. HOMO would play an important role in the reaction to follow. Obviously, the reactivity of isobutane is dependent upon the activity of the hydrogen atom (H14).

The 2-butene protonated by strong acids is fully optimized and the C16 atom becomes saturated. The length of C15–C16 bond increases from 0.1388 to 0.1438 nm, and the C15–C18 bond length shortens slightly to 0.1449 nm. By comparing the changes of charge, it is found that C15 atom has a large charge value (0.5041*e*), while other carbon atoms possess increasing negative charges. This shows that C1 has strong Lewis acidity, suggesting that C15 can react with groups or reagents with negative charges.

As R_{H14C15} distance between the two atoms decreases, the energy curve (see Fig. 3-1) of the reaction descends first and the



model 1-1: protonated butene acting with isobutane **model 1-2: tert-butyl cation acting with butene**

Fig. 1. Two calculation models. Model 1-1: protonated butene reacting with isobutane. Model 1-2: *tert*-butyl carbonium ion reacting with butene.