

Reaction mechanism of ionic liquid catalyzed alkylation: Alkylation of 2-butene with deuterated isobutene



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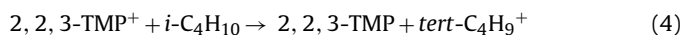
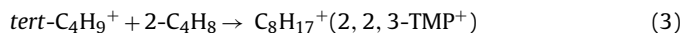
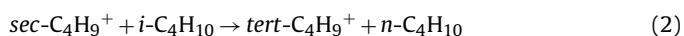
ABSTRACT

The ionic liquid catalyzed alkylation of 2-butene with deuterated isobutane was studied in a continuous flow equipment. Product analyses with time and deuterated distribution determinations were obtained. It is found that the induction period of ionic liquid alkylation is much shorter than that of sulfuric acid. A considerable difference in isobutane solubility between ionic liquid and sulfuric acid was observed with ionic liquid having a greater tendency to dissolve isobutane at the start-up of alkylation. Deuterated product distributions indicate that trimethylpentane fractions stemmed primarily from the self-alkylation of isobutane, the direct alkylation reaction of C₄ hydrocarbons, and the scission of C₁₂⁺ intermediates. Most dimethylhexanes should come from the direct addition of *sec*-butyl carbonium ions to 2-butenes.

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1. Introduction

The acid catalyzed alkylation of butenes with isobutanes is an important process in the petrochemical industries. The products from a sulfuric or hydrofluoric acid alkylation reactor consist of a mixture of mono-methyl, di-methyl, and tri-methyl alkanes. Of these, the tri-branched octanes are the most desired ingredients in gasoline because they have high octane numbers. In order to improve the yield and selectivity of iso-octanes in alkylate, the alkylation mechanism of protonic acids (*i.e.*, H₂SO₄ and HF) has been studied for many years. C₄ alkylation reaction is believed to proceed *via* a carbonium ion mechanism [1–3]. First, rapid protonation of 2-butene to *sec*-butyl carbonium ion (*sec*-C₄H₉⁺) followed by the hydride transfer between isobutane and *sec*-C₄H₉⁺ forms *tert*-butyl carbonium ion (*tert*-C₄H₉⁺) and *n*-butane. The resulting *tert*-C₄H₉⁺ reacts rapidly with 2-butene to produce trimethylpentane cation (TMP⁺), which is converted to 2,2,3-trimethylpentane (2,2,3-TMP) *via* hydride transfer from isobutane. A new *tert*-butyl carbonium ion is generated during the hydride transfers process and another reaction cycle starts. A general reaction scheme for isobutane/2-butene alkylation can be summarized as follows:



Albright [4–6] has proposed a more complete reaction scheme when H₂SO₄ is used as a catalyst. The reactions of butyl sulfates as well as the role of acid-soluble hydrocarbons are considered in the global scheme. When hydrofluoric or trifluoromethanesulfonic acid was used to catalyze isobutanes and isobutylenes, a detailed reaction pathway was described by Olah et al. [7,8]. Density functional theory and *Ab initio* method have also been employed to determine the reaction mechanism of C₄ alkylation [9,10]. The results of theoretical calculation tended to support the classic mechanism assumption that 2-butene is rapidly protonated to form *sec*-C₄H₉⁺, and then reacts with isobutane to form *tert*-C₄H₉⁺. The resulting carbonium ion is deprotonated to form isobutene that reacts rapidly with *tert*-C₄H₉⁺ to form TMP⁺.

Ionic liquids (ILs) as new catalysts have shown many interesting properties [11,12]. For instance, the most important properties of C₄ alkylation may be the acid strength and the solubility of isobutane in the acid [13]. But for ILs, these properties can be readily tuned by using different organic cations or inorganic anions [14–17]. Additionally, many ILs can maintain high catalytic activity during the whole alkylation reaction without carbon deposition problems as compared to solid acid alkylation. Some ILs have been reported for the pilot-scale alkylation test [11]. However, few studies have been devoted to the reaction mechanism of IL catalyzed alkylation reaction. One possible reason may be that the alkylation reaction process is complex because of the simultaneous reactions including olefin polymerization, protonation, and cracking.

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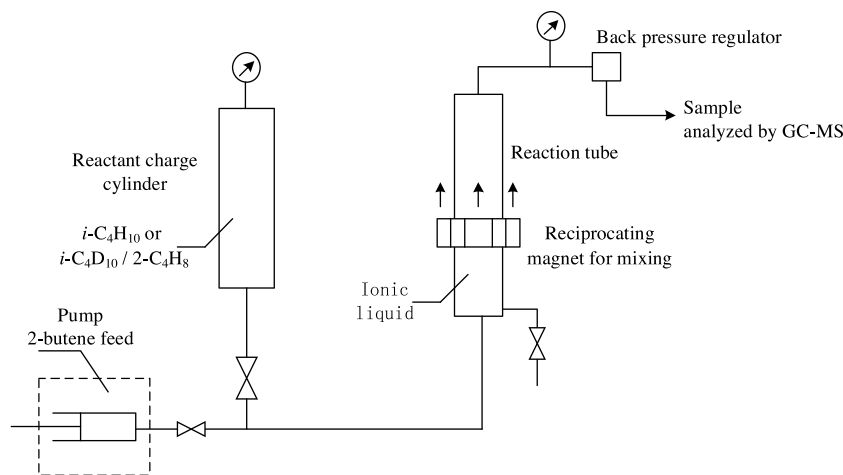


Fig. 1. Continuous flow reactor for C₄ alkylation.

The difficulty in detecting the intermediates under the rigorous reaction conditions also leads to the alkylation mechanism of ILs has not been validated [18]. On the other hand, almost all of previous research works on both the alkylation reaction and the role of ILs had been carried out in batch reactors, in which the acid was contacted with the isoparaffin-olefin and the entire mixture analyzed at the end of the reaction. It is almost impossible to detect the intermediates and to study the reaction mechanism by the product distribution over time [19].

There are some experimental results of IL alkylation indicating that the classical reaction mechanism cannot provide a full explanation. For example, when chloroaluminate ILs are used as catalysts as compared to H₂SO₄ alkylation, a short contact time between the acid phase and feed is favored [20,21]. If a composite IL [22,23] or a Brønsted-Lewis acidic IL [16] is employed under the optimal operating conditions, the alkylate will contain about 5–10 wt% C₅–C₇ compounds (light ends) and 5–10 wt% compounds of higher molecular weight (heavy ends). Particularly, the most valuable trimethylpentanes are often greater than 80 wt%. These results from the point of view of product distributions are far superior to those of traditional acids.

The aim of this paper is to study the reaction mechanism of IL catalyzed C₄ alkylation through experimental measurements of reaction. Two ionic liquids, [BMIm]Cl-AlCl₃ and [BMIm]-AlCl₃-CuCl, were used as catalysts. The approach adopted in this investigation was to utilize flow equipment, in which the reaction could be followed as a function of time, and the product distributions with time could be obtained. In addition, deuterated isobutane (i-C₄D₁₀) was used as an isoparaffin feed and a tracer to react with 2-butenes. By means of analyzing the deuterated product distributions, a relatively easy way was found to investigate the reaction mechanism. A better understanding of the chemistry of C₄ alkylation might help explain the formations of trimethylpentanes, light ends, and heavy ends in different ionic liquids.

2. Experimental

The chloride salt of the 1-butyl-3-methyl-imidazolium cations ([BMIm]Cl) was obtained from Sigma-Aldrich Chemical Company and dried under vacuum at 100 °C. [BMIm]Cl-AlCl₃ ionic liquid (BIL) and [BMIm]Cl-AlCl₃-CuCl (composite ionic liquid, CIL) were prepared and characterized using methods as early described [17]. In this work, the mole ratios of AlCl₃ and CuCl to organic salt are 1.6:1 and 0.4:1, respectively. Isobutane and 2-butene were commercial products from China National Petroleum Corporation (CNPC) with 99% purity and used without further purification. Deuterated

isobutane (i-C₄D₁₀, 98%) was obtained from Cambridge Isotope Laboratories, Inc.

Experimental work was carried out in a small continuous flow reactor, as shown in Fig. 1. A typical experiment is performed in the following manner. After purging the entire system with nitrogen, the ionic liquid is charged to the reaction tube (over-all length 12 cm, inside diameter 1.5 cm) to a level about 5 cm above the bottom, so that it completely fills the reaction zone. The feed is a premixed 2-butene/isobutane (or deuterated isobutane) blend with a mole ratio of i-C₄H₁₀/C₄H₈ of approximately 7/1. The feed of hydrocarbon flows from the reactant charge cylinder and is catalyzed by IL in the reaction tube. The hydrocarbon-acid emulsion is disengaged in the top of the reaction tube and the hydrocarbon is depressurized and then vaporized to analyze. The total hydrocarbon sample is periodically analyzed on a gas chromatograph (Hewlett-Packard, 6890 Series II) equipped with a mass spectrometer (Hewlett-Packard, 5972 Series II column). The initial ionic liquid charge remains in the reactor for the duration of the experiment.

Studies on the induction period were carried out in the same reactor using method as literature [24] described. Isobutane and 2-butene were all gas-phase feeds. In a typical experiment, the IL/isobutane mixture was put into the reactor at first and the reactor was initially at atmospheric pressure. After mixing to assure saturation of the IL with isobutane, 2-butene was pumped into the reactor at a constant rate (e.g. 10 mL/min). Meanwhile, the consumption of isobutane with time was measured by observing the input of isobutane required to maintain a constant pressure (e.g. 140 kPa, absolute pressure) in the reactor.

3. Results and discussion

3.1. Induction period and the alkylate components with time

Stewart and Calkins have measured the induction period of the sulfuric acid alkylation by observing the gaseous isobutane consumption [24]. We determined the induction period of the IL alkylation using the similar method. Fig. 2 shows the results made during a typical experiment. Both IL alkylation processes all have an induction period, during which little or no isobutane is used. However, the induction period of IL alkylation is less than 4 min, which is far shorter than that of H₂SO₄ alkylation. Table 1 lists the product distributions at the induction period, the steady state period, and the terminal reaction period, respectively. The BIL and CIL product distributions have a marked difference at the induction period. The CIL alkylate contains more C₈ compositions, however, the content of C₁₂ is also higher than that of BIL. During the steady state and

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