REGULAR ARTICLE

DFT Study of the Catalytic Mechanism for Urethane Formation in the Presence of Basic Catalyst 1,4-diazabicyclo[2.2.2]octane

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Abstract： In this work, the catalytic mechanism for urethane formation between isocyanate groups and alcohols was examined. The reaction of methanol with methylisocyanate and 2, 4-toluene diisocyanate in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) basic catalysts was simulated using density functional theory (DFT) methods at B3LYP/6-31+G(d, p) level. The DABCO catalysis of the reaction between isocyanates and methanol was shown to proceed in two steps. Firstly, the hydrogen transferred from the hydroxyl group of alcohols to the nitrogen atom of DABCO. Secondly, the hydrogen showed rapid migration from the nitrogen atom of DABCO to the nitrogen atom of the isocyanate group. The calculated energy barrier for the reaction of methanol with methylisocyanate and 2, 4-toluene diisocyanate was determined at 17.2 and 14.1 kcal·mol^{-1}, respectively, which was in a good agreement with the experimental data of 10.8-16.7 kcal·mol^{-1}. The activation energy required for urethane formation was significantly reduced in the presence of DABCO. The results also indicated that a larger basis set, including diffusion and polarization functions, is required to obtain an accurate energy barrier for urethane formation.

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1. Introduction

Polyurethane materials were first developed in the 1930s from isocyanates and alcohols. The two most commonly used classes of isocyanates in polyurethane coatings are aliphatic and aromatic isocyanates. Due to their versatility, polyurethanes have become an essential part of the modern life [1]. Organic bases and organometallic catalysts are widely used in the polyurethane applications [2-5]; for instance, the tertiary amines, such as 1,4-diazabicyclo[2.2.2]octane(DABCO), are commonly used in urethane formation [6-8]. An understanding of the catalytic mechanism is essential for more precise management of the reaction.

Previous theoretical studies have described a concerted process in the reaction of isocyanates and polyols where alcohol addition occurs across the C=N bond and immediately results in the urethane product [9-12]. More recent calculations also show that self-catalysis by alcohol is characterized by urethane formation without additional catalysts [12]. Moreover, Samuilov examined the reaction between methyl isocyanate and linear methanol associates at B3LYP/6-311++G (df, p) level and found that the activity of the reacting system increases with the degree of methanol association [11]. Çoban and Konuklar [13] determined that the reaction of *n*-butanol with aromatic diisocyanates is more likely to occur in a concerted path than in a stepwise fashion, where an energy barrier of about 40 kcal·mol^{-1} was reported. In addition, Tilo Söhnel recently proposed a mechanism for urethane formation in the presence of organotin (IV) carboxylate [14]. Moreover, Hatanaka described urethane formation with tertiary-amines as a catalysts at level B3LYP/3-21G, where catalytic urethane formation with DABCO was characterized as an accelerated direct addition [15]. It has been established that the energy of the urethanation reaction is strongly dependent on the applied functional basis set, which should contain at least one diffusion function in the simulation for proper realization of the thermo-chemical features in the urethane formation reaction. In our calculations, methylisocyanate(MeNCO) and 2,4-toluene didsocyanate are used to model the aliphatic and aromatic isocyanates, respectively. To provide accurate results, the amine catalysis of urethane formation between methylisocyanate, 2,4-toluene didsocyanate (2,4-TDI) and methanol is studied at B3LYP/6-31+G (d, p) level. A different energy barrier and mechanism are depicted for the urethane catalysis of DABCO. At level B3LYP/6-31+G (d, p), it is proposed that the catalytic urethane formation with DABCO will follow two steps, as shown in Scheme 1. First, the proton transfers from alcohol, such as methanol, to the catalyst DABCO. Then, a meta-stable intermediate forms. Secondly, the proton moves from DABCO to the -NCO group of isocyanates of methylisocyanate and 2,4-TDI, after which the urethane finally forms. At level