Interaction between trialkyltin alkoxide and phenyl isocyanate in the formation of tin carbamate: A computational and experimental study

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ABSTRACT

Organotin catalysts are used to catalyze the reaction of isocyanates and alcohols in the manufacture of urethanes. Therefore it is important to understand the mechanism of the catalysis to get a greater control of the reaction to obtain specific properties of the final product. Until now the proposed mechanism related to organotin catalysis of urethane formation is based on the mechanism suggested by Bloodworth and Davies (1965) on the reaction between trialkyltin alkoxide and phenyl isocyanate. In the present work computational and experimental methods were used to investigate the interaction between trialkyltin alkoxide and phenyl isocyanate. The computational results agree with the experimental results reported by Bloodworth and Davies. The computational investigation also provided further insight into the interaction mechanism. The investigations indicate that initially the isocyanate oxygen is attracted towards the tin atom of the organotin alkoxide, which subsequently undergoes an insertion reaction to form an organotin O-carbamate (methyl tributylstannyl phenylcarbonimidate), which rearranges to form an organotin N-carbamate (methyl phenyl(tributylstannyl)carbamate). Model compound studies of the urethane formation in the presence of trialkyltin catalyst using ^{13}C NMR and FT-IR data show that the reaction goes through a termolecular mechanism. This is also confirmed by comparing reaction rates between trialkyl and dialkyl tin as catalyst at similar tin content for the reaction between aromatic isocyanate and alcohol and comparing with computationally calculated intrinsic reaction coordinate profile of different transition states for similar interactions.

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1. Introduction

Polyurethanes are formed by the reaction between a polyisocyanate and a polyol. They are major groups of polymers used in products such as coatings, adhesives, elastomers and composites [2]. However, as in most chemical reactions, catalysts are used in practical applications of polyurethane synthesis. Despite that, several types of catalysts have been used in the polyurethane industry [3]. Amongst them, organotin compounds are the most commonly used catalysts due to outstanding efficiency. Therefore, to understand the mechanism of organotin compounds in the catalytic process of the urethane synthesis has become important for the advancement of the polyurethane industry. The organotin catalysis of urethane formation has been intensively investigated [1,4–11]. Bloodworth and Davies [1] have reported that trialkyltin methoxide

will readily react with phenyl isocyanate to undergo an insertion reaction to give tin carbamate as shown in Scheme 1.

The reaction has provided information on how organotin catalysts catalyze urethane formation between isocyanate and alcohol. The mechanism suggests that catalysis takes place through an insertion reaction by the interaction of the isocyanate and an organotin alkoxide that is formed as a result of alcoholysis of an organotin compound. Apart from this mechanism two other mechanisms have also been proposed: an ionic mechanism and a Lewis acid mechanism [12]. However, out of the three proposed mechanisms the insertion mechanism has gained more interest compared to the others. Based on this information the mechanism of organotin compounds on the catalysis of urethane formation has been reviewed [12–14]. It seems possible that the mechanism of the reaction differs depending on the type of tin catalyst used as well as the relative concentrations of both the catalyst and reagents. In spite of all the efforts that have been put into elucidating the reaction mechanism of organotin in urethane formation the complete mechanism still remains unknown. In this paper we have investigated the reaction mechanisms using a computational chemistry

Tributyltin Methoxide   Phenyl isocyanate   methyl phenyl(tributylstannyl)carbamate
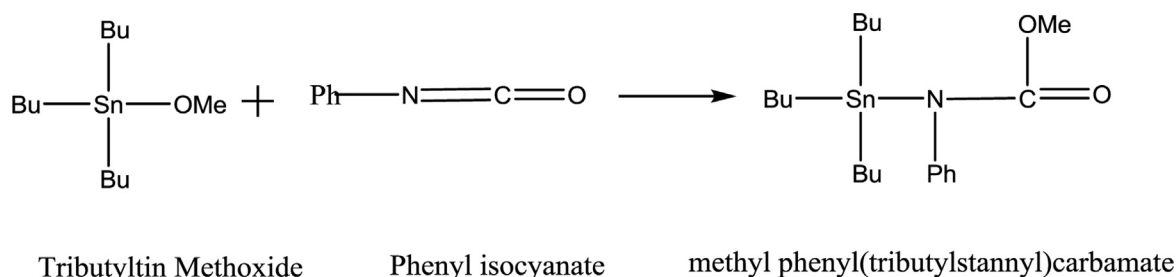
Scheme 1. Interaction between TBTM and phenyl carbamate.

approach. Computational methods have already been used to investigate reactions between isocyanate and alcohol groups [15–21]. The urethane formation in the presence of a catalyst has only been reported for tertiary amines [22,23], however little effort has gone into investigating urethane formation in the presence of organometallic compounds, metal salts or metal chelates. In the study presented in this paper the interaction between trialkyltin alkoxide and aromatic isocyanate was investigated using computational methods to gain insight into the reaction mechanism. Once the mechanism was selected the hypothesis was tested against new experimental data. We believe that this will clear most of the unknown in the reaction mechanism and provide information to design new catalysts that are more efficient and less toxic to the environment.

2. Experimental

2.1. Computational details

Very recently we have investigated urethane catalysis in the presence of organotin carboxylate catalyst using computational methods [24]. In this work we have tested the DFT B3LYP functional and *ab initio* MP2 level of theory with basis sets 6-31G*, 6-31G** and 6-31+G** for all light elements and LANL2DZ for tin atom in different solvent environments to simulate the interaction between organotin compounds, isocyanate and alcohol. The computational approach given in this paper has also been applied in the present investigation and the results are reported here. In the present investigation the interacting centers of the two molecules are brought together step by step while optimizing the energy at each step using a selected level of theory. The energy profile of the interaction will give information related to mechanism. In the following work the DFT/B3LYP LANL2DZ/6-31G* level of theory is selected unless specified. From these simulations approximate transition states were obtained and refined using the Berny algorithm [25] until one negative frequency was obtained in all cases. Then it is verified by relating to product and reactants using an intrinsic reaction coordinate approach [26,27]. Steps are also taken to check the effect of the polarity of a solvent on reactivity and mechanism by using the CPCM model [28,29] and water as polar solvent and toluene as non-polar solvent. In this work we used model compounds such as phenyl isocyanate, methyl isocyanate, methyl alcohol, trimethyltin methoxide (TMTM) and dimethyl tin dimethoxide (DMTDM) to model aromatic and aliphatic isocyanates, polyol, tributyltin methoxide (TBTM) and dibutyltin dibutoxide (DBTDB), respectively. Computational work was carried out using the Gaussian 09 [30] and Spartan 10 [31] computational software programs. All calculated energies are reported as electronic energies at 0 K unless specified. The values reported as free energies and enthalpies include zero point correction at 298 K.

2.2. Experimental work on reactivity of isocyanate and alcohol in the presence of organotin compound as catalyst

Isocyanates were reacted with alcohols in various quantities in the presence of organotin compounds as catalysts in xylene and THF. The total volumes of the reaction mixtures were made to the same volumes. The amounts of tin in the reaction mixtures were maintained at constant levels unless specified in all experiments. Samples were withdrawn at regular intervals and the free isocyanate content in the reaction mix was determined according to the ASTM D2572-97 method [32]. In this method isocyanate first reacted with a known amount of dibutylamine then the isocyanate content was determined by titrating excess amine with standard solution of hydrochloric acid.

Desmodur 44 V 20 L (Bayer, Germany) were used as aromatic isocyanate. Tributyltin methoxide (TBTM) 97% was obtained from Sigma chemicals. Dibutyltin dibutoxide (DBTDB) was obtained from Gelest Inc., USA and dibutyltin dilaurate (DBTDL) was obtained from Air Products (USA). Phenyl isocyanate, reagent grade 1-butanol, 2-butanol, tert-butanol, THF and xylene (all Merck, Germany) were used without further purification. Isocyanate was reacted with varying amounts of alcohol at 25 °C in an appropriate solvent in the presence of selected catalysts. In this set of experiments the isocyanate amount was maintained at 0.279 equiv. and stoichiometric amounts of alcohol was reacted in the presence of varying amounts of tin catalyst as specified in different solvents. The total volume of the starting reaction mix was maintained at 183 mL.

3. Results and discussion

3.1. Interaction between tributyltin methoxide and phenyl isocyanate

The interaction between tributyltin methoxide and phenyl isocyanate was simulated using trimethyltin methoxide and phenyl isocyanate to reduce computational costs. The interaction between trimethyltin methoxide and phenyl isocyanate was simulated using two different starting orientations of the isocyanate molecule:

(1) Orientation of isocyanate oxygen directed towards tin center.
(2) Orientation of isocyanate nitrogen directed towards tin center.

Fig. 1 shows the orientation of the isocyanate molecule in the two simulations.

Fig. 2 shows the energy profile of the interactions for the initial orientations of the isocyanate molecule where the nitrogen atom is directed towards the tin atom. In the simulation the oxygen atom of the methoxy group and the carbon of the isocyanate group were brought together step by step while minimizing the total energy of the system. In Table 1 the molecular structures associated with the interactions are shown in Fig. 2. It is interesting to see that when