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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.

AMS subject classifications: 92E10, 80A30

Keywords: MeNCO, 2,4-TDI, DABCO, Urethane Formation, DFT

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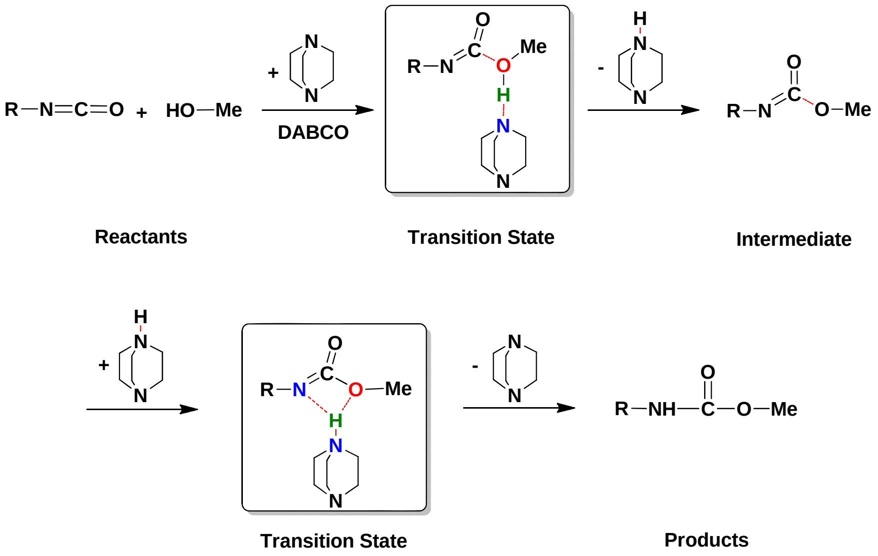
1. Introduction

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

B3LYP/3-21G, an intermediate on the shallow potential minimum is missed, and the calculated energy barrier of 5.6 kcal·mol^{-1} is much lower than that determined in the experimental data of similar reactions at 10.8-16.7 kcal·mol^{-1} [16]. It is therefore evident that a larger basis set including diffusion and polarization functions is required for an improved energy barrier in urethane formation.



Scheme 1. The two-step urethanation between isocyanates and methanol.

2. Computational Details

Due to its computational simplicity and reasonable accuracy, the Kohn-Sham density functional theory has been widely utilized in the investigation of a variety of molecular properties in a wide range of systems, such as equilibrium structure, charge distribution, reaction barrier in chemistry and binding energy in drug design [17-19]. In the present work, the catalytic mechanism of urethane formation in the presence of DABCO was examined using density functional theory at level B3LYP/6-31+G(d, p). All of the electronic structure calculations were performed using the Gaussian 09 suite [20]. Optimization in the geometries of the reactants, intermediates, transition states (TS) and products was achieved using the density functional theory (DFT) with level B3LYP/6-31+G(d, p) [21-23]. Based on the optimized geometries, a frequency analysis was performed to verify the characters of the transition states with one imaginary frequency and stationary points without imaginary frequency [24-26]. An intrinsic reaction coordinate (IRC) calculation was performed in both forward and reverse directions, and the energy profile connecting each TS to the two associated minima of the proposed mechanism was confirmed [27]. To obtain the accurate energy barrier, zero point energy (ZPE) corrections were used to estimate relative energy barriers.

3. Results and Discussion

3.1 DABCO Catalytic Reaction between Methylisocyanate and Methanol

Aliphatic and aromatic isocyanates are the two main classes of isocyanates used in polyurethane coatings. The main application of aliphatic isocyanates is in the manufacture of light-stable coatings. To simplify the calculations, methylisocyanate was used to model the aliphatic isocyanates in the DABCO catalytic reaction. **Figure 1** shows the optimized geometries of the reactants（**1**）and（**2**）, catalyst（**3**） and products (**4**). The corresponding total energies, including zero point energies, are summarized in **Table 1**. The catalyst DABCO is known as a very good nucleophile with a pair of unshared electrons and is favorable for the attack of a nucleus. In the reaction between methylisocyanate and methanol, a nucleophile DABCO first attacks on the hydrogen of methanol, and a stable pre-reaction complex forms with a hydrogen bond between the nitrogen of DABCO and the hydrogen of the hydroxyl group, as shown in **Figure 2**. The hydrogen in the hydroxyl group of methanol carries a positive charge of 0.487, which is slightly larger than the charge 0.340 of the isolated methanol. This can be attributed to the strong polarization from the nitrogen of DABCO, as illustrated in **Figure 2**. In addition, the nitrogen atom of DABCO and oxygen atom of the hydroxyl group possess greater negative charge of -0.519 and -0.561 than the charge of -0.184 and -0.528 of isolated molecules respectively. A strong hydrogen bond with a distance of 1.83Å can significantly reduce the total energy of the pre-reaction complex 5 by 10.1 kcal·mol^{-1}, as compared to the separated reactants shown in **Table 2**. Following nucleophilic interaction of the DABCO molecule along the hydroxyl group of the methanol, the transition state TS6 developed with one 377i cm^{-1} imaginary frequency as shown in **Figure 2**. Here, the hydrogen of hydroxyl group was shared by the nitrogen atom of the catalyst DABCO and the oxygen atom of the methanol molecule, which was located 17.2 kcal·mol^{-1} above the energy of the pre-reaction complex **5**. The stable intermediate **7** was located through IRC analysis for forward direction. IRC confirmed that **TS6** was connected with intermediates **5** and **7**. As illustrated in **Figure 2**, the hydrogen of the hydroxyl group was transferred from the methanol molecule to the nitrogen atom of DABCO. Meanwhile, the oxygen of methanol, with an excess of electrons (-0.496), nucleophilically attacked the carbon atom of the isocyanate group, with a charge of 0.508, leading to a fixture between two electronegative oxygen and nitrogen atoms to form a new C-O bond. The corresponding total energy was thus slightly reduced by -0.51 kcal·mol^{-1} relative to that of **TS6** as summarized in **Table 2**.

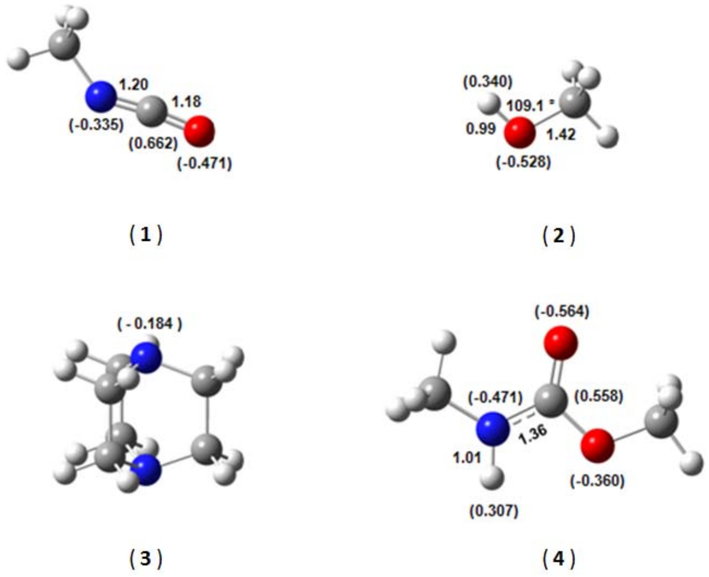
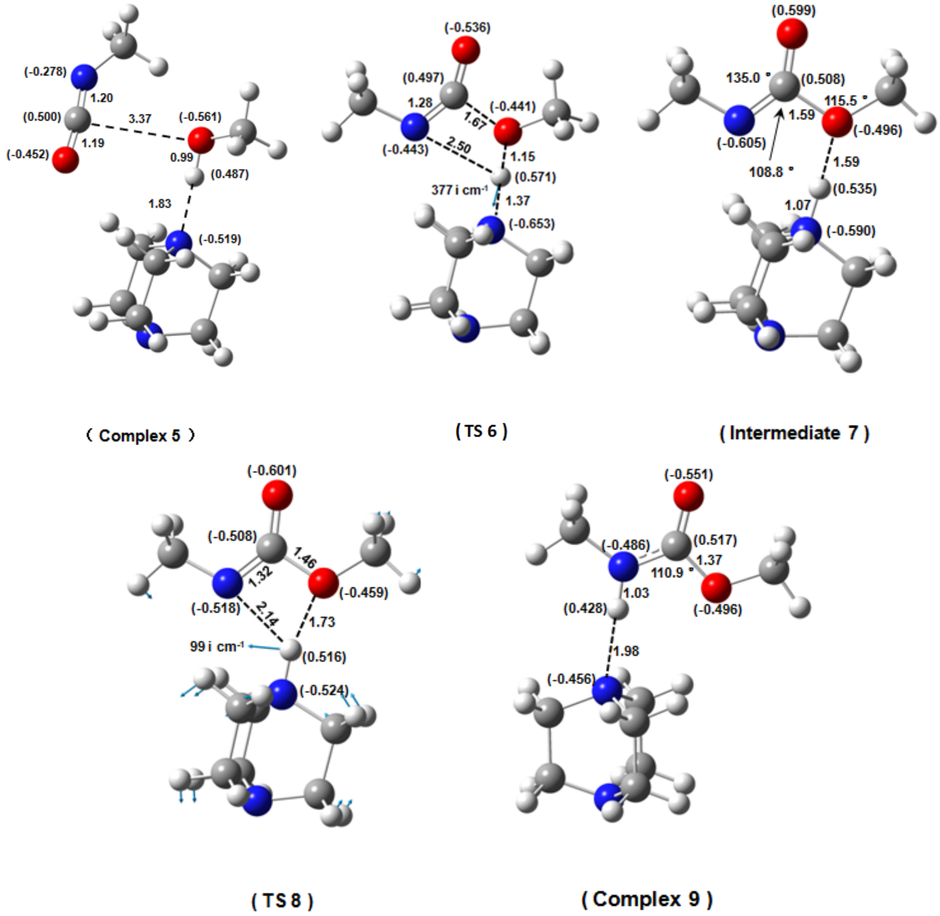


Figure 1: Optimized geometries of (**1**) MeNCO, (**2**) methanol, (**3**) DABCO, and (**4**) the urethane product. Mulliken charges are labeled in parentheses.

Table 1. The total and ZPE energies (Hartree) of (**1**) MeNCO, (**2**) methanol, (**3**) DABCO, and (**4**) the urethane product.

Compound Name	Total Energy	ZPE
MeNCO	-207.95102	0.05056
Methanol	-115.68364	0.05124
DABCO	-345.17122	0.18315
Urethane product	-323.66811	0.10736

For intermediate **7**, the reaction continued via transition state **8**. This was characterized by a -NHCO- four-membered ring with an imaginary frequency 99i cm^{-1} in addition to the nitrogen of isocyanate group with a mulliken charge of -0.518 that nucleophilically interacted with the hydrogen of the hydroxyl group of methanol with a positive charge of 0.516, as shown in **Figure 2**. A small amount of activation energy of 0.17 kcal·mol^{-1} was obtained relative to stable intermediate **7**, which indicated that the proton transfer from the nitrogen of DABCO to the nitrogen of the isocyanate group was a relatively fast process. For the forward reaction, the transition state **TS8** led to the urethane-DABCO complex **9**, where the proton transferred from the nitrogen of DABCO to the nitrogen of isocyanate group, which led to urethane formation. **Figure 3** illustrates the relative energy profile of the reaction between methylisocyanate and methanol in the presence of the catalyst DABCO. As shown in **Figure 3**, the reaction followed a two-step mechanism. Firstly the hydrogen of the hydroxyl group of methanol transferred to the nitrogen atom of DABCO with an energy barrier of 17.2 kcal·mol^{-1}. Then, the hydrogen migrated from the DABCO to the isocyanate group of methylisocyanate with a relatively low barrier of 0.17 kcal·mol^{-1}. The non-catalytic reaction of methylisocyanate with methanol was investigated by Samuilov at B3LYP/6-311G++(df,p) level using Gaussian 03 software, where the activation energy barrier was estimated at 32.5 kcal·mol^{-1} [11]. The reaction barrier of methylisocyanate with methanol was significantly reduced to 17.2 kcal·mol^{-1} in the presence of catalyst DABCO, which is in accordance with experimental data 10.8-16.7 kcal·mol^{-1} for the similar reactions [16].



(Complex 5) (TS 6) (Intermediate 7)

(TS 8) (Complex 9)

Figure 2: Optimized structures of complex **5**, **TS6**, intermediate **7**, **TS8** and urethane complex **9** for the reaction between MeNCO and methanol with DABCO serving as a catalyst. Mulliken charges are labeled in parentheses.

Table 2. The total (Hartree) and relative (kcal·mol^{-1}) energies of optimized structure for the reaction between MeNCO and methanol with DABCO serving as a catalyst, all corrected by zero-point vibrational energies (ZPE).

Optimized Geometry	Total Energy	Relative Energy
MeNCO+MeOH+DABCO	-668.80588	0
Complex 5	-668.82205	-10.14
TS6	-668.79468	7.02
Intermediate 7	-668.79549	6.52
TS8	-668.79521	6.69
Urethane complex 8	-668.84774	-26.26
Urethane+DABCO	-668.83933	-20.98

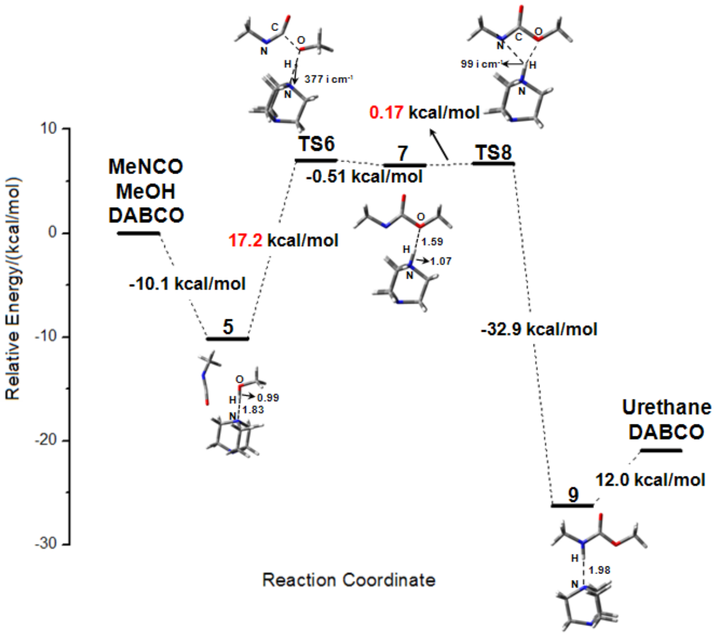
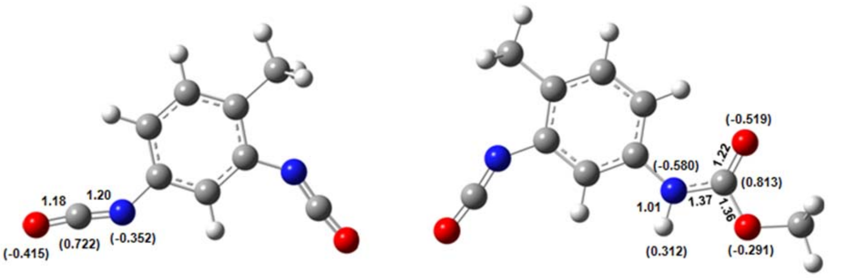


Figure 3: The profile for the reaction between methylisocyanate and methanol with DABCO catalysts

3.2 DABCO Catalytic Reaction between 2,4-TDI and Methanol

Next, the effects of aliphatic and aromatic isocyanates on the reaction activity were studied. Thus, 2,4-toluene didsocyanate (2,4-TDI), as a typical aromatic isocyanate that is widely used as a chemical intermediate in the production of polyurethane products such as foams, coatings, and elastomers, was utilized. Our attention turned to the DABCO catalytic reaction between 2,4-TDI and methanol. The two isocyanate groups in TDI reacted at different rates but maintained a similar reaction mechanism. The reaction was calculated between the isocyanate group at 4-position with methanol. **Figure 4** illustrates the optimized geometries of the reactant 2,4-TDI and urethane product. **Table 3** lists the total energies including zero point energies. The reaction between methylisocyanate and methanol began with a nucleophilic attack of DABCO on the hydrogen of methanol. A stable pre-reaction complex **12** subsequently formed with a strong hydrogen bond between DABCO and methanol as shown in **Figure 5**. The hydrogen of the hydroxyl group of methanol carried a positive charge of 0.493, while the nitrogen atom of DABCO carried a negative charge of -0.517. The total energy of pre-reaction complex **12** was dramatically reduced by 10.7 kcal·mol^{-1}, which was in sharp contrast with the separated reactants. As the DABCO molecule nucleophilically approached along the hydroxyl group of the methanol, the transition state **TS13** with one 170i cm^{-1} imaginary frequency was formed, as illustrated in **Figure 5**. Here, the hydrogen of the hydroxyl group was shared between the catalyst DABCO and the methanol molecule, which was located 14.1 kcal·mol^{-1} higher than the energy of the pre-reaction complex **12**. By performing the IRC analysis in a forward direction, the stable intermediate 14 was determined. As indicated in **Figure 5**, the hydrogen of the hydroxyl group transferred from the methanol molecule to the nitrogen atom of DABCO. Meanwhile the oxygen of methanol, with an excess of electrons (-0.391), simultaneously attacked the carbon atom of the isocyanate group with a charge of 0.689, forming a new C-O bond with a distance of 1.45 Å. The total energy was lowered by -3.87 kcal·mol^{-1} in contrast to TS13 as summarized in **Table 4**.



(**10**) (**11**)

Figure 4: Optimized structures of (**10**) 2,4-TDI and (**11**) the urethane product. Mulliken charges are labeled in parentheses.

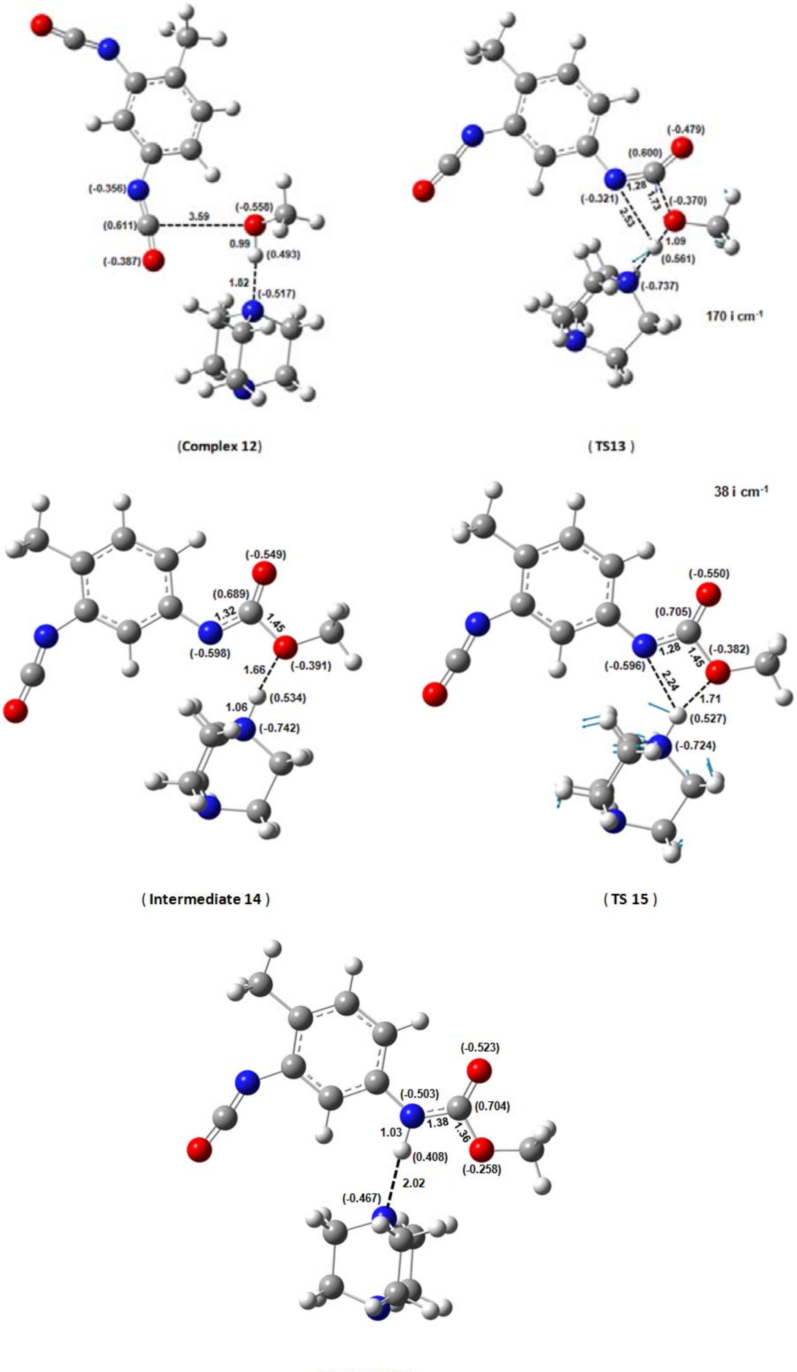
From intermediate **14**, transition state **15** was formed, which was characterized by an -NHCO- four-membered ring with an imaginary frequency 38i cm^{-1}, as shown in **Figure 5**. A similar structure to intermediate **14** was displayed in **Figure 5** with a small activation energy barrier of 0.028 kcal·mol^{-1}. Moreover, the proton demonstrated rapid transfer from the nitrogen of DABCO to the nitrogen of the isocyanate group. According to the IRC calculation, the transition state **TS15** led to the urethane-DABCO complex **16** where the proton was transferred from the nitrogen of DABCO to the nitrogen of the isocyanate group. **Figure 6** depicts the relative energy profile for the reaction between 2,4-TDI and methanol in the presence of the catalyst DABCO. As illustrated in **Figure 6**, the reaction proceeded in two steps. Firstly, the hydrogen transferred from the hydroxyl group to the nitrogen atom of DABCO with an energy barrier of 14.1 kcal·mol^{-1}, which was consistent with the experimental data in similar reactions at 10.8-16.7 kcal·mol^{-1} [16]. Then, the hydrogen rapidly migrated from DABCO to the isocyanate group. As in the reaction between methylisocyanate and methanol, the first step occurred at a limited rate, while the second step of proton transfer occurred rapidly. From a comparison between the energy barrier of methylisocyanate with 2,4-TDI and methanol, it is evident that the 2,4-TDI was more active than the methylisocyanate.

Table 3. The total and ZPE energies (Hartree) of (**10**) 2,4-TDI, (2) methanol, (**3**) DABCO and (**11**) the urethane product.

Compound Name	Total Energy	ZPE
2,4-TDI	-606.42970	0.13437
Methanol	-115.68364	0.05124
DABCO	-345.17122	0.18315
Urethane product	-722.14464	0.19111

Table 4. The total (Hartree) and relative (kcal·mol^{-1}) energies of optimized structure for the reaction between 2,4-TDI and methanol with DABCO as a catalyst, all corrected by zero-point vibrational energies (ZPE).

Optimized Geometry	Total Energy	Relative Energy
2,4-TDI+MeOH+DABCO	-1067.28456	0
Complex 12	-1067.30162	-10.70
TS13	-1067.27908	3.43
Intermediate 14	-1067.28526	-0.44
TS15	-1067.28522	-0.41
Urethane complex 16	-668.84774	-25.50
Urethane+DABCO	-668.83933	-19.64



(Complex 12) (TS13)

(Intermediate 14) (TS 15)

(Complex 16)

Figure 5: Optimized structures of complex **12**, **TS13**, intermediate **14**, **TS15** and urethane complex **16** for the reaction between 2,4-TDI and methanol with DABCO as a catalyst. Mulliken charges are labeled in parentheses

In the non-catalytic reaction of 2,4-TDI with methanol, the energy barrier was estimated at 27.21 kcal·mol^{-1} at level B3LYP/6-311G(d,p) [28]. Activation energy was drastically reduced compared with reactions in the absence of DABCO, indicating that DABCO was an effective catalyst for polyurethane formations.

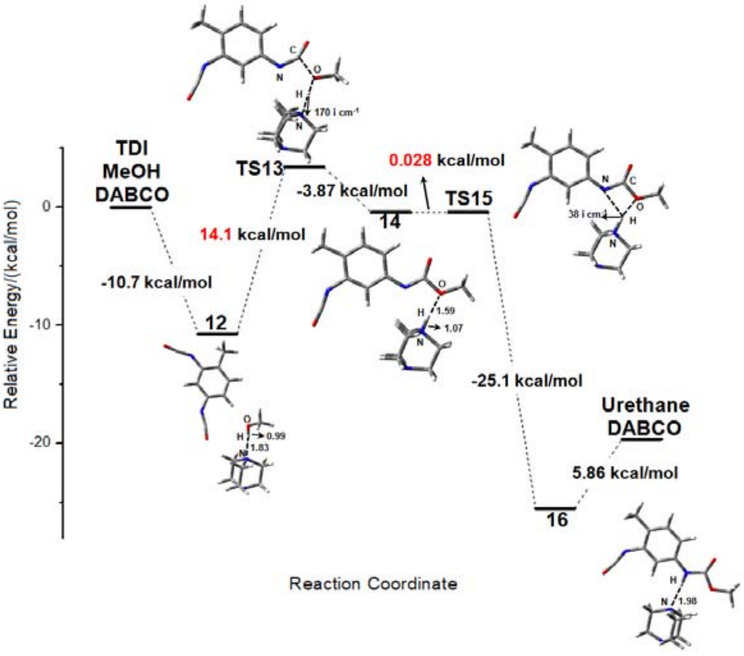


Figure 6: The profile for the total reactions between 2,4-TDI and methanol with DABCO catalysts

In summary, a catalytic urethane formation method with DABCO has been depicted under two steps at B3LYP/6-31+G (d, p) level. Firstly, protons from alcohol, such as methanol, transferred to the catalyst DABCO to form a meta-stable intermediate. Secondly, the protons moved from DABCO to the -NCO group of isocyanates such as methylisocyanate and 2,4 TDI, immediately forming the urethane. The calculated energy barriers for the reaction of methanol with methylisocyanate and 2, 4-toluene diisocyanate were determined at 17.2 and 14.1 kcal·mol^{-1}, respectively, which was in accordance experimental data for similar reactions at 10.8-16.7 kcal·mol^{-1} [16]. Thus, the 2,4-TDI was more active than the methylisocyanate. Using B3LYP/3-21G level [15], an intermediate on a shallow potential minimum was missed; and the calculated energy barrier of 5.6 kcal·mol^{-1} was much lower than the experimental data at 10.8-16.7 kcal·mol^{-1} [16]. A larger basis set, including diffusion and polarization function, is required to obtain an accurate energy barrier for the urethane formation reaction.

4. Conclusions

Urethane formation between methylisocyanate, 2, 4-toluene diisocyanate and methanol in the presence of the basic catalyst DABCO was investigated using density functional theory at the B3LYP/6-31+G (d, p) level. The catalytic urethane formation proceeded in two steps. Firstly, the hydrogen transferred from the hydroxyl group of alcohols to the nitrogen atom of DABCO. Then, the hydrogen migrated quickly from the nitrogen atom of DABCO to the nitrogen atom of the isocyanate group. The calculated energy barrier for the reaction of methylisocyanate, 2, 4-toluene diisocyanate and methanol was determined at 17.2 and 14.1 kcal·mol^{-1}, respectively, which was in accordance with the experimental data of similar reactions at 10.8-16.7 kcal·mol^{-1} [16]. Moreover, it was determined that 2,4-TDI was more active than methylisocyanate. Activation energy was drastically reduced compared with reactions in the absence of DABCO, indicating that DABCO was an effective catalyst for polyurethane formations. In comparison with previous results obtained from the B3LYP/3-21G level, a larger basis set, including diffusion and polarization functions, was required to obtain an accurate energy barrier for the urethane formation reaction.

Acknowledgements

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