RSC Advances

RSC Advances

www.rsc.org/advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

Organotin carboxylate catalyst in urethane formation in polar solvent: An experimental and computational study

Ransi Devendra,[a] Neil R. Edmonds[a] and Tilo Söhnel[a,b,]*

Organotin carboxylates are important catalysts in aliphatic urethane synthesis. They are widely used in two component urethane systems such as casting systems, high performance coatings and in the synthesis of one-component moisture cure urethane pre-polymers for coatings. In most of these systems, a solvent is used to reduce the viscosity to assist application. In general, aromatic hydrocarbon solvents such as xylene, R100 or oxygenated solvents (e.g. esters) are used. In this paper, a detailed investigation of the catalytic mechanism of organotin carboxylate in urethane synthesis in a polar medium is investigated using experimental and computational methods. There is evidence that the dominant catalyst for organotin carboxylate catalysis of aliphatic isocyanate in urethane formation in a polar medium is organotin alkoxide. In this work, DFT studies on B3LYP / LANL2DZ/6-31+G** level of theory with the CPCM solvent model was used to study the reactivity between isocyanate and alcohol in the presence of selected organotin catalyst in different mediums. The theoretical studies were supported by experimental evidence.

1. Introduction

The first investigation of catalysis of aromatic isocyanate in urethane formation by organotin carboxylate was carried out in 1965 by Boodworth and Davis[1]. Since then many investigations have been carried out to study the mechanism of urethane formation with organotin compounds used as catalysts[2-8]. Most of these works were carried out using aromatic isocyanates. Based on these investigations, three different types of mechanisms for the catalysis have been suggested: 1) Insertion mechanism (organotin alkoxide)[1]; 2) Lewis acid mechanism[10] and 3) Ionic mechanism[5], with the insertion/organotin alkoxide mechanism being the most popular (Scheme S1). In the ionic mechanism it is claimed[1,2,9] that for the organotin carboxylate catalysis of urethane, an alkoxide is formed as an intermediate which becomes the dominant catalyst. Solvent effects on urethane formation in the presence of organotin carboxylate catalyst are also reported in literature[6], this is different to the alkoxide mechanism. The reason to put forward different mechanisms may be due to the type of medium that was used in the experimentation. However, these mechanisms were also used to explain the catalysis of aliphatic isocyanate in urethane formation. Organotin carboxylates have become important in aliphatic urethane synthesis[11], they are widely used in two-component urethane systems, e.g. casting systems, high performance coatings etc.[12,13]. Nevertheless, the proposed mechanisms were satisfactory for solving industrial problems related to most of these products. Consequently,

very few investigations had been carried out on organatin carboxylate catalysis in urethane formation since the above-mentioned investigations. However, with the development in the demand for high performance coatings and adhesives, urethane pre-polymers have become important in the polyurethane industry. These pre-polymers are urethane polymers with active isocyanates as functional end-groups. Organotin carboxylate catalysts are used in the synthesis of moisture cure urethane aliphatic pre-polymers for coating applications. In most of these systems, a solvent is used to reduce the viscosity to assist the application of the polyurethanes. In general, aromatic hydrocarbons solvents, such as xylene or R100 etc., or oxygenated solvents such as esters are used. Since these pre-polymers contain active isocyanate functional groups and catalysts, the long-term stability becomes important.
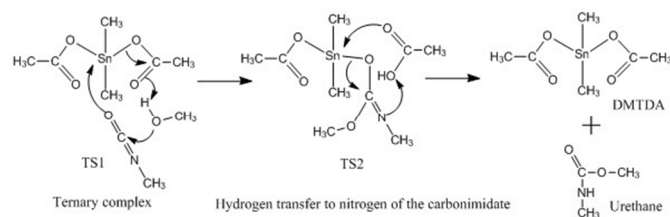
Scheme 1. Computationally proposed mechanism for organotin carboxylate catalyzed urethane formation for aliphatic system.

Knowledge of the mechanism of how the catalyst functions in different solvent environments is important in the preparation of pre-polymer for long-term storage and its film formation after application. Computational chemistry has been used intensively to study mechanisms of chemical reactions. Computational methods were already used in investigating the reaction mechanism of urethane formation[14-20], mainly to investigate the reaction between isocyanate and alcohol groups. Applications to elucidate the reaction mechanism of urethane formation in the presence of catalyst has only been reported by a few researchers[21,22,23]. The application of computational methods to model the interaction between an organotin compounds and isocyanate and alcohol groups in urethane formation has been discussed previously[24] and mechanisms for urethane catalysis by organotin carboxylate in non-polar media were proposed. It was shown that for aliphatic systems the carboxylate ligand contributes to the catalysis, Scheme 1 shows the mechanism. However for an aromatic system the carboxylate ligand has lesser effect. In our recent publication[24] the effect of polar media on the reaction rate of urethane formation in the presence of organotin carboxylate catalyst was discussed briefly. In the present paper, the urethane formation in the presence of organotin carboxylates catalyst were carried out in polar medium and compared to non-polar media. In this set of experiments, oxygenated solvents were used as polar media. The results are discussed with the help of computational work to establish the details of the reaction mechanism. The experimental work considered both aliphatic and aromatic isocyanates. However, more emphasis was given to aliphatic isocyanates where organotin carboxylates are mostly used as catalysts. Based on these investigations, mechanisms were proposed for the organotin carboxylate catalysis of aliphatic and aromatic isocyanates in urethane reactions in polar solvents.

2. Experimental

2.1 Computational methods

In the present work, computational methods similar to what was discussed in previous publications are followed. In the simulations, model compounds such as DMTDA (dimethyltin diacetate), DMTMA (dimethyltin methoxy acetate), methyl alcohol, methyl isocyanate, and phenyl isocyanate were used to keep the computational costs to a minimum. Simulations were done by decreasing the distance between the interacting centres while optimizing the total energy of the system, details of the method are given in the publication[24]. From these energy profiles, approximate transition states were estimated and then they were optimized using the Berny algorithm[25]. The transition states were further verified with respect to reactance and product by determine the intrinsic reaction coordinates. Intrinsic reaction coordinate plots are used to extract data related to proposed mechanisms[26]. Unless otherwise specified, in this work a DFT/B3LYP/LANL2DZ/6-31+G** level of theory was used for energy calculations, with the CPCM solvent model being applied to describe toluene or water as the non-polar

and polar solvents[9,24]. The calculations were carried out using the Gaussian 09 and Spartan 14 software packages[27,28]. All energies are reported as electronic energy at 0 K unless otherwise specified. Gibbs free energies and Enthalpies are reported at 298 K as difference respect to starting material. $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ correspond to the difference in Enthalpy and Gibbs free energy from the first local minimum before the transition state in the energy diagram.

2.2 Statistical modeling

Two-level factorial is a modelling method practiced in design of experiments to study the effect of input variables on a selected response[29]. These effects are studied by determining the variance of the response by changing the input variable within a pre-determined range in a systematic way (F-test in statistics). Since the input variable is changed between two selected upper and lower values, the technique is called two level factorial design. In our study, a two-level full factorial method was used and the experiments were carried out by changing the input variables in all possible combinations. Results show the effect of each variable and the interaction between these variables on a selected response. The results are interpreted using Design Expert[30] statistical software. The changes in the average effect are plotted in a half normal plot, which separates the variables that significantly influence the response from the rest. The interacting graphs show the interaction between variables to a selected response.

2.3 Materials used

N-butanol, *sec*-butanol, *tert*-butanol, phenyl isocyanate, acetic acid, xylene, 1-methoxy-2-propylacetate were obtained from Merck, Germany, 1,3-dioxolane from Ferro Corporation USA and DBTDA (dibutyltindiacetate) from Air products, USA, DBTDB (dibutyltindibutoxide 95%) from Gelest Inc., USA, Desmodur N 3390, Desmodur N 3600 and Desmodur L75 from Bayer, Germany. All reagents were used as received without any further purification.

2.4 Investigation of reaction rate between isocyanate and alcohol

Stoichiometric amounts of isocyanate and alcohol were reacted at 25°C in solvents as specified in the presence of selected catalysts. Initially 0.279 equivalents of Desmodur N 3390 was reacted with n-butanol in the presence of 0.4 g of catalyst (2.8% DBTDA/xylene) or as specified. The total initial volume of the reaction mix was maintained at 183 mL. When 0.279 equivalent of Desmodur L 75 was used as the isocyanate, the total volume was maintained as 172 mL. Isocyanate was reacted with n-butanol in the presence of 0.4 g of catalyst (2.8% DBTDA/xylene) or as specified. Xylene, 1-methoxy-2-propyl acetate and 1,3-dioxolane were used as solvents in these experiments. In all reactions the total tin content was kept the same. When DBTDB + acetic acid (1:1mole) was used as the catalyst first the mix was allowed to react before using as the catalyst. Samples were drawn from the reaction mix at 10 minutes intervals and the weight %NCO (isocyanate) was determined as to the method specified in ASTM D 2572-97[31].

2.5 NMR Spectroscopy

^{13}C-NMR spectra for samples were obtained for compounds made in CDCl$_3$ solutions, using a Bruker 400MHz spectrometer.

2.6 Two level factorial to identify the effect of solvent type, urethane groups, DBTDA and DBTDB on final viscosity

Statistical two-level factorial design of experiments was used to detect the effects of selected variables in a system on a selected response. Statistical experimental design analysis was carried out with four variables i.e. concentration of DBTDA, DBTDB and n-butanol with Desmodur N3600 as the isocyanate in two solvent medium (xylene and 1,3dioxolane as non-polar and polar media). Samples were prepared by first mixing 150 g of Desmodur N36000 in 50 g of solvent. Each ingredient (n-butanol, DBTDA and DBTDB) was varied in the range 5-10g, 0.175-0.53g and 0.2-0.6 g, respectively. The total tin content was maintained at the same level. The viscosity was measured after one day and after 3 weeks storing at 40°C.The results were analysed using Design Expert software[30].

3. Results and Discussion

3.1 Aliphatic isocyanate

3.1.1 Reactivity study in different conditions

Figure 1 shows the depletion of the NCO (isocyanate) content with time for the reaction between Desmodur N3390 and n–butanol in different media in the presence of DBTDA catalyst. From the figure it can be seen that the reaction in the polar media (1,3-dioxolane and 1-methoxy-2-propyl acetate) is higher than if the reaction is carried out in non-polar media (xylene), which can be estimated from the gradient of the plot. It is also seen that there is a significant difference in reaction rate between 1-methoxy-2-proply acetate and 1,3-dioxolane. It is known that 1-methoxy-2-propyl acetate consist of lower levels of free acetic acid as an impurity. Therefore the effect of acetic acid at lower level with 1,3-dioxolane was tested, and an increase in reaction rate for the combination of 1,3-dioxolane and acetic acid compared to 1,3-dioxolane can be found. The effect of acetic acid at lower level on organotin caboxylate in urethane formation of aliphatic isocyante will be discussed in a separate publication. The intention was to explain the reason for the significant difference in the reaction rate between 1,3-dioxolane and 1-methoxy-2-propyl acetate. Figure 2 shows the catalytic action of DBTDA and DBTDB + acetic acid (1:1 mole) as catalyst in 1,3-dioxolane and xylene for the reaction between Desmodur N3390 and n-butanol. In these reactions, the concentration of tin in each reaction was maintained the same and the total volume of the reaction was maintained at 183 mL. It can be seen that when DBTDA and its alkoxy derivatives were used as catalysts for aliphatic systems, the reaction rate depends on the type of medium the reaction takes place in. In non-polar medium (xylene) alkoxy derivative has a lesser effect compared to DBTDA, and the effect is opposite in polar (1,3-dioxolane) medium. The overall higher reaction rate in 1,3-dioxolane for DBTDA may be due to the formation of alkoxy derivatives as suggested in literature[9]. This suggests a change in mechanism.
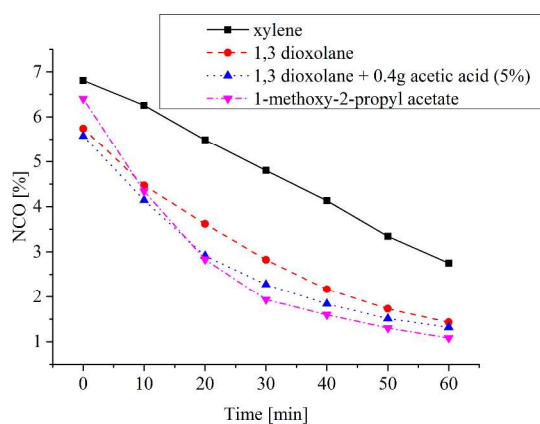

Figure 1. Reaction between Desmodur N 3390 and n-butanol as stoichiometric amounts in different solvents with 0.4 g DBTDA (2.8% in xylene) used as catalyst.
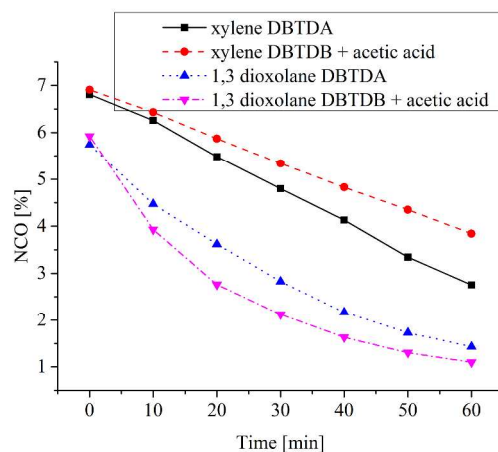

Figure 2. Effect of different catalyst combinations in urethane formation in different solvent media, 0.4 g DBTDA (2.8% in xylene), and DBTDB + acetic acid (1:1mole) (3.6% in xylene)

Figure 3 shows the reaction between Desmodur N3390 and n-butanol in different solvents at constant volume (183 mL), using DBTDA as the catalyst. The reaction rate changes when the OH:NCO (alcohol : isocyanate) ratio change from 1:1 to 2:1 (equivalents ratio) depending on the solvent. The NCO level depletion rate with changing OH:NCO ratio is different in xylene when compared to the reaction in 1,3-dioxolane as the medium. This suggests that the catalytic mechanism for DBTDA may be different in xylene to 1,3-dioxolane. This may be due to conversion of DBTDA to its alkoxy derivative. The reaction in 1,3-dioxolane as the medium shows a higher catalytic action towards the end of the reaction with increasing OH:NCO ratio. The effect of the alcohol concentration on the reactivity of aliphatic and aromatic isocyanate in the presence of organotin carboxylate catalyst in non-polar solvent are reported in our previous publication[24]. These results show that the catalytic behaviour for aliphatic isocyanate is different to aromatic isocyanate, which indicate that they have two different mechanisms in non-polar systems.
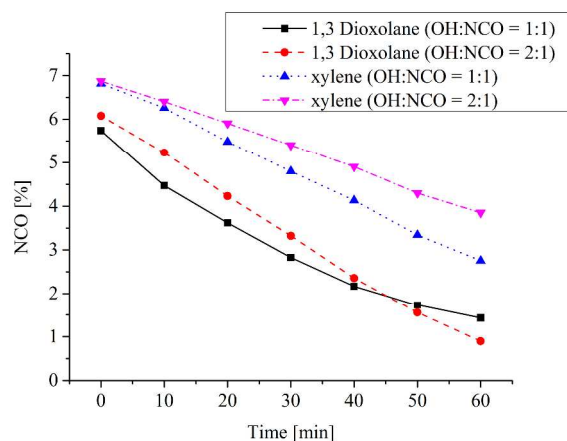
Figure 3. Effect OH:NCO ratio on reactivity between n-butanol and Desmodur N3390 with DBTDA (2.8% in xylene) used as catalyst in different solvents.

3.1.2 Effect of organotin compounds and polarity of the solvent on the stability of urethane pre-polymers

This investigation was carried out to understand the stability of urethane pre-polymer system when synthesised using organotin compounds as catalyst in polar and non-polar solvents, respectively. Figure 4 shows the half normal plot of the effects with respect to viscosity after ageing the system in the oven at 40°C for three weeks. From the figure it can be seen that the factors DBTDB and n-butanol are the greatest contributors to the viscosity. It is also seen that the polarity of the media also contribute to increase in viscosity of the system. This may be due to the stabilizing effect of organotin alkoxide in polar media that will lead to polymerization of isocyanate. This result confirms the effects that were shown from the previous reactivity studies in different media as in Figure 2.
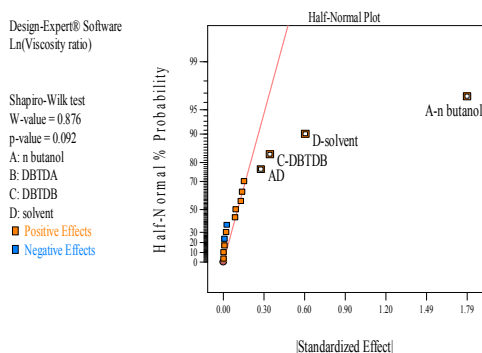

Figure 4. Half normal plot for the effects on viscosity as a response.

3.2 Aromatic isocyanate

3.2.1 Reactivity study in different conditions

Figure 5 shows the depletion of the NCO content with time for the reaction between Desmodur L75 and n-butanol at stoichiometric amounts in the presence of organotin compound with different amounts of carboxyl ligand content in 1,3-dioxolane as the media. It

can be seen that the reaction rate does not depend on the level of carboxyl ligand content. The tin content in the reaction was similar in all experiments. This was similar to what was observed when the reaction was carried in xylene as shown previously[24]. These results indicate that for an aromatic system the organotin alkoxide is the dominant catalyst. Figure 6 shows the reaction between Desmodur L75 and n-butanol in different solvents when organotin carboxylate is used as a catalyst and it is clear that the reaction rate in xylene is higher than in 1,3-dioxolane. This is due to the high activation energy in polar media as explained previously[24]. However, this effect is opposite to what was observed for aliphatic isocyanates. These effects will be further discussed in computational section.
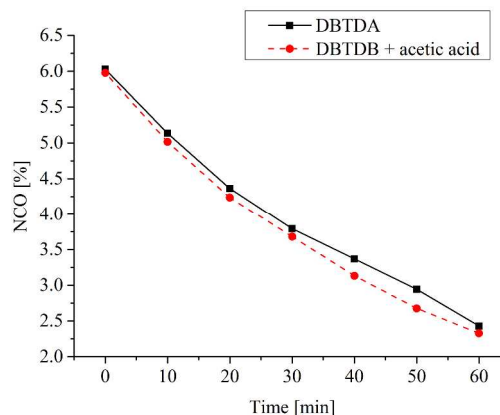

Figure 5. Depletion of NCO content for the reaction between Desmodur L75 and n-butanol in 1,3-dioxalan in the presence of different organotin compounds. 0.4 g DBTDA (2.8% in xylene) and 0.4 g DBTDB + acetic acid (1:1mole) (3.6% in xylene).
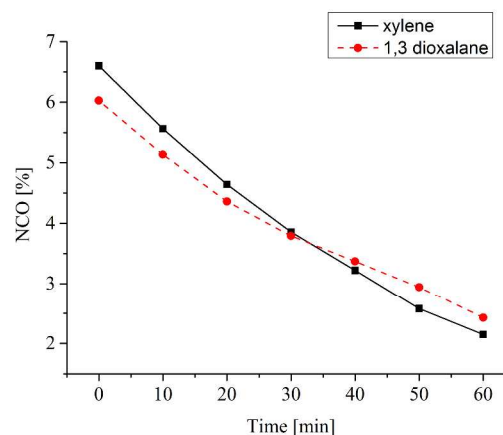

Figure 6. Depletion of NCO content when Desmodur L75 reacted with n-butanol in xylene and 1,3dioxolane in the presence of 0.4 g DBTDA (2.8 % in xylene) as catalyst.

3.3 Reactivity of aliphatic and aromatic isocyanate in the absence of organotin catalyst

Figure 7 shows the interaction between aliphatic and aromatic isocyanate and n-butanol in the presence of different additives. The interaction between aliphatic isocyanate and alcohol was not

reported because of its very low reactivity. However, the use of acetic acid at lower concentrations has no significant effect in urethane formation for both aromatic and aliphatic isocyanate. Aromatic isocyanate has a higher reactivity in non-polar solvents.
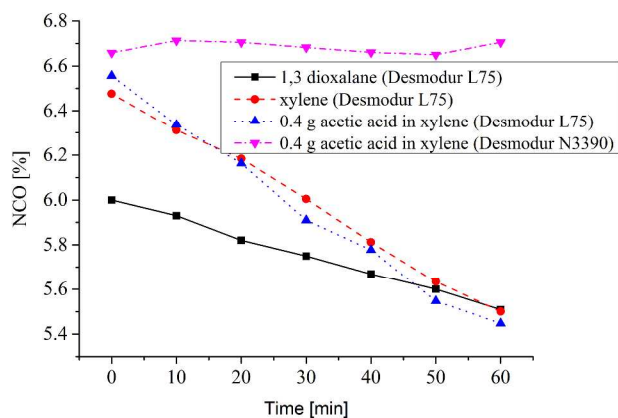
through Sn-N coordination, it should result in only one type of urethane, i.e. urethane with n-butoxy as that alkoxy urethane. Since the sample has an additional peak due to the urethane of the corresponding alcohol that was used in the initial reaction mix, the reaction should follow the mechanism previously proposed[24].
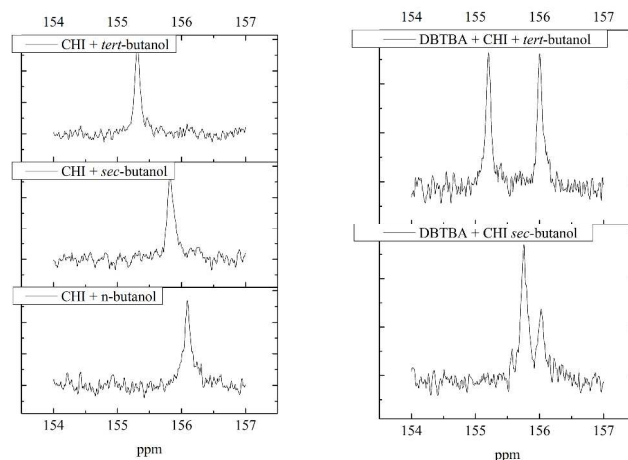

Figure 7. Reactivity between DesnoducL75, Desmodur N3390 and n-butanol in different solvent with acetic acid (5% xylene).

3.4 ^{13}C NMR analysis of reaction products for aromatic isocyanate

The following experiments were carried out as evidence for a ter-molecular mechanism in urethane formation in the presence of organotin alkoxide catalyst.

3.4.1 Reaction products for aliphatic isocyanates

DBTBA (dibutyltin butoxy acetate) was synthesised as described in the literature by reacting molar quantities of DBTDB with DBTDA at 60°C overnight. The product was used without further purification[32]. It is reported in literature that it is possible to identify urethane groups that have structural differences using ^{13}C NMR spectroscopy[33]. Reaction products of DBTBA, cyclohexyl isocyanate and alcohol (1:1:1) and DBTDB, cyclohexyl isocyanate and alcohol (1:2:2) were analysed using ^{13}C NMR spectra in CDCl$_3$ as solvent. In this experiment the organotin alkoxide was initially mixed with alcohol by the addition of the isocyanate. Figure 8 (left) shows the ^{13}C NMR spectra for urethane carbon for each reaction product n-butanol, *sec*-butanol and *tert*-butanol with cyclohexyl isocyanate at 156.090, 155.822 and 155.314 ppm, respectively. Figure 8 (right) shows the ^{13}C NMR spectra for the reaction products of different starting mixtures using DBTBA. ^{13}C NMR urethane carbon resonances of the reaction product of DBTBA + *sec*-butanol + CHI and DBTBA + *tert*-butanol + CHI at (1:1:1) moles can be found at 156.09, 155.76 and 156.00, 155.2 ppm, respectively, and the urethane carbon resonance of the reaction product of DBTDB + *sec*-butanol + CHI and DBTDB + *tert*-butanol + CHI at (1:2:2) moles at 156.00, 155.75 and 156.00, 155.20 ppm, respectively. It can be seen that each spectrum shows two peaks due to the product formation. However, as explained before, if the interaction is between the alkoxy oxygen of the organotin compound and the isocyanate

Figure 8. ^{13}C NMR for urethane carbon ; a) CHI + n-butanol, b) CHI + *sec*-butanol and c) CHI + *tert*-butanol (left). ^{13}C NMR spectra for urethane carbon for the reaction products; a) DBTBA + CHI + *sec*-butanol; b) DBTBA +CHI + *tert*-butanol (right).
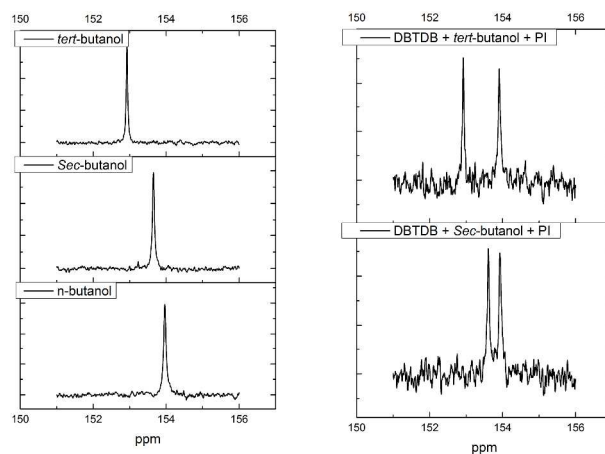

Figure 9. ^{13}C NMR spectra for urethane carbonyl carbon for phenyl isocyanate reacted with n-butanol, 2-butanol and *tert*-butanol (left); ^{13}C NMR for DBTDB and PI reacted with 2-butanol and *tert*-butanol at 1:2:2 mole ratio (right).

3.4.2 Reaction products for aromatic isocyanate

Similar to the aliphatic isocyanate studies, investigations were carried out with phenyl isocyanate and by using organotin alkoxide in urethane formation. Figure 9 (left) shows the ^{13}C NMR spectra of the urethane carbonyl reaction between n-butanol, *sec*-butanol and *tert*-butanol with phenyl isocyanate at 153.965, 153.654 and 152.928 ppm, respectively. Figure 9 (right) shows the ^{13}C NMR spectra of

the reaction products of DBTDB + *sec*-butanol + PI and DBTDB + *tert* butanol + PI at 1:2:2 mole ratios. When *sec*-butanol was used, the spectra show both the urethane carbonyl carbon of n-butanol and *sec*-butanol. Similarly, *tert*-butanol shows the urethane carbonyl carbon of n-butanol and *tert*-butanol. From these spectra it is clear that phenyl isocyanate has reacted with free alcohol. This evidence supports the mechanism proposed[24] for organotin alkoxide catalysed urethane reaction for phenyl isocyanate.

4 Computational work

In this work, a DFT B3LYP / LANL2DZ / 6-31+G** level of theory was used in the calculations, with the CPCM solvent model to describe water as the polar medium and toluene as non-polar medium. In all energy diagrams, the van der Waals complexes on the product side are not shown for clarity. In the modelling work for methyl isocyanate catalysis with DMTDA in the urethane formation, the interaction between methyl isocyanate and DMTDA is taken as O-coordinated. It is noticed that with increasing the size of the alkyl group connected to tin atom, steric effect are more probable for N-coordination interaction than for the O-coordination.

4.1 Aliphatic isocyanate

Figure 10 shows the energy profile of the reaction between methyl isocyanate and methyl alcohol when DMTDA is used as a catalyst in polar medium. The first minimum shows the formation of the hydrogen-bonded methanol Sn-complex proceeded by the interaction with the isocyanate molecule to form the ternary van der Waals complex. This first minimum is shown in all energy diagrams. Enthalpies and Gibbs free energies differences for TS1 are $\Delta H_{298} = 86.94$ and $\Delta G_{298} = 197.93$ kJ mol^{-1} ($\Delta H^{\ddagger} = 80.75$ kJ mol^{-1}, $\Delta G^{\ddagger} = 132.97$ kJ mol^{-1}), respectively. TS1 is the transition state for the formation of organotin carbonimidate. Enthalpy and Gibbs free energy difference for TS2 are $\Delta H_{298} = 23.32$ and $\Delta G_{298} = 130.13$ kJ mol^{-1} ($\Delta H^{\ddagger} = 1.19$ kJ mol^{-1}, $\Delta G^{\ddagger} = 12.26$ kJ mol^{-1}), respectively. TS2 represents the transition state for the conversion of organotin carbonimidate to urethane and DMTDA. The total change in enthalpy and Gibbs free energy with respect to starting material to product in pathway 1 is -85.37 and -34.18 kJ mol^{-1}. Reaction steps are shown in Scheme 1 for pathway 1. The TS1 energies calculated (single point) using DFT / M06-2X / LANL2DZ / 6-31+G** level of theory with CPCM solvent model in water, are $\Delta H_{298} = 13.44$ and $\Delta G_{298} = 128.75$ kJ mol^{-1} ($\Delta H^{\ddagger} = 30.34$ kJ mol^{-1}, $\Delta G^{\ddagger} = 64.26$ kJ mol^{-1}), respectively, indicating a significant difference between the functional used ($\Delta H = 73.5$ kJ mol^{-1}, $\Delta G = 69.18$ kJ mol^{-1}, $\Delta S = 14.5$ J K^{-1}mol^{-1} between the different levels of theory). It is claimed[34,35] that the meta-hybrid functional M06-2X gives more accurate thermochemical data for main group compounds. The TS1 energies were also calculated (single point) using DFT/B3LYP/ LANL2DZ / cc-pVTZ level of theory with CPCM solvent model in water, resulting in $\Delta H_{298} = 78.90$ and $\Delta G_{298} = 190.70$ kJ mol^{-1}, respectively, indicating a small basis set effect ($\Delta H = 8$ kJ mol^{-1}, $\Delta G = 7.2$ kJ

mol^{-1}, $\Delta S = 2.8$ J K^{-1}mol^{-1} between the different levels of theory). TS3 is the transition state for the conversion of organotin carbonimidate to urethane and DMTMA as in Scheme 2. The enthalpy and Gibbs free energy for this transition are $\Delta H_{298} = 14.25$ and $\Delta G_{298} = 123.56$ kJ mol^{-1} ($\Delta H^{\ddagger} = 2.13$ kJ mol^{-1}, $\Delta G^{\ddagger} = 11.35$ kJ mol^{-1}), respectively. The total change in Enthalpy and Gibbs free energy with respect to starting material to product in pathway 2 is -61.04 and -10.63 kJ mol^{-1}, respectively.

Figure S1 shows the intrinsic reaction coordinate plots of the transition states TS1, TS2 and TS3 for the interaction between DMTDA, methanol and methyl isocyanate. The curvature of the plots gives an indication of the forward reaction for the interaction. It is also seen in the simulation that the detached acetic acid molecule stays close to the tin centre. Figure 11 shows the structure of both the intermediates formed in the non-polar and polar media. The equilibrium distance between the acetic acid and the tin atom will depend on the polarity of the medium. It can be seen that in a polar medium the equilibrium distance (5.63 Å, Figure 11 left) is shorter than in non-polar (6.03 Å, Figure 11 right) medium. Therefore, in a polar medium, the probability of the acetic acid moving out of the centre without further participation in the reaction is somewhat higher. In both scenarios, the acetic acid is hydrogen bonded with the alkoxy oxygen connected to the isocyanate carbon. Also, the calculation results did not show the two molecules (e.g. the organotin alkoxide and acetic acid) in two disjointed cavities. The transition state energy TS1 in polar and non-polar medium has also been reported in our previous publication[24]. These data show that in polar medium has a higher TS1, transition state energy when compared to non-polar medium. Therefore the catalytic effect in polar medium for aliphatic should be slower than in non-polar medium, However, as to Figure 1, it is seen that the catalytic effect for urethane formation in the presence of DBTDA is higher in polar (1,3-dioxolane) solvents than in non-polar (xylene) solvent. This data suggest that it is possible to undergo a change in the mechanism due to a change in the composition of the organotin carboxylate catalyst after TS1, without regenerating the organotin carboxylate.
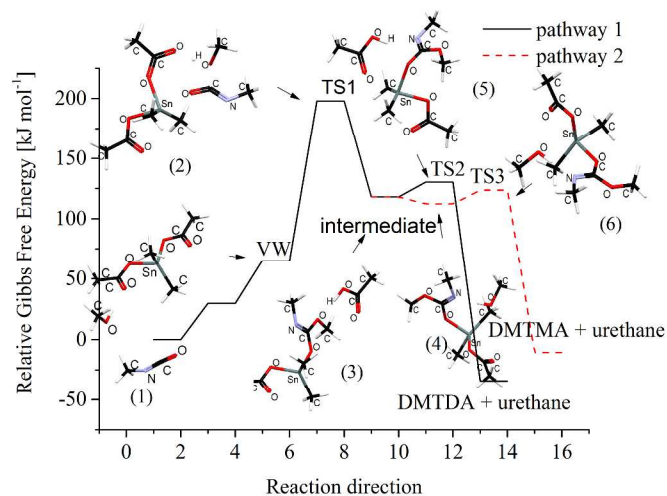

Figure 10. Energy diagram for the methyl isocyanate and methanol catalyzed with DMDTA in water as the polar medium.
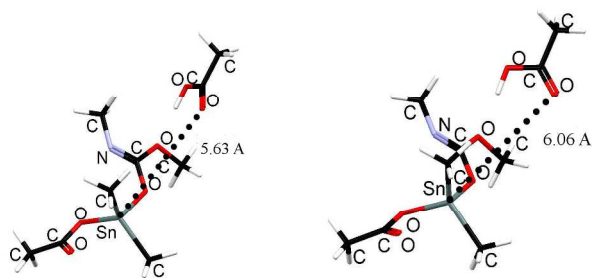
Figure 11. The equilibrium intermediate structure in toluene (left) and water (right).

Figure 13 shows the hydrogen-bonded acetic acid to 1,3-dioxolene and to the tin catalyst, respectively. The enthalpy and Gibbs free energy differences for the association of the two assemblies of the tin catalyst and 1,3-dioxolane are ΔH_{298} = -0.57 kJ mol^{-1}, ΔG_{298} = 41.26 kJ mol^{-1} and ΔH_{298} = -17.60, ΔG_{298} = 28.71 kJ mol^{-1}, respectively. The interaction between acetic acid and the structure formed as the intermediate and 1,3-dioxolane were calculated in polar medium. This suggests that there is a high probability that the acetic acid will move into the medium.
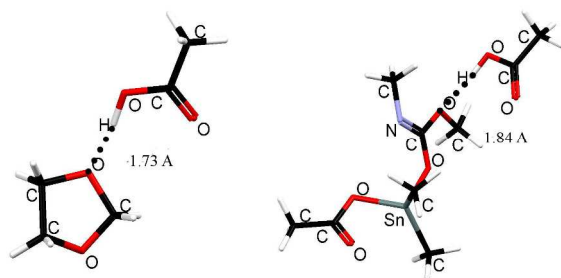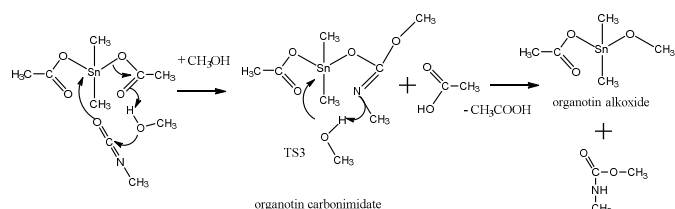
Figure 12. Hydrogen bonded 1,3-dioxolane and acetic acid (left); acetic acid hydrogen bonded to tin carbonimidate (right).

Scheme 2. Organotin alkoxide formation from organotin carboxylate.
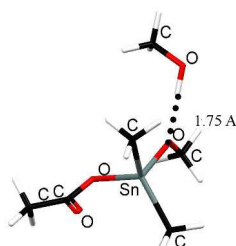
Figure 13. Van der Waals complex formed between DMTMA and methanol in polar medium.

In the catalysis reaction, the alcohol will be present in excess of the catalyst. Therefore it is possible that all organotin alkoxide is converted to the corresponding alkoholate. Therefore, dimethyltin methoxy acetate that is formed after TS3 will get coordinated with methanol to form an alkoholate; the structure of the alkoholate is shown in Figure 13.

4.2 Organotin alkoxide catalysis of isocyanate

The formation of the alkoxide intermediate in polar medium was discussed in the previous section. It is also suggested that this alkoxide will be alkoholated in the presence of a high concentration of alcohol in the medium. Therefore in the following discussion the interaction between isocyanate and the alcoholised organotin alkoxide will be discussed.

4.2.1 O-coordinated interaction of the isocyanate

The interactions between alcoholated organotin alkoxide, methyl isocyante and methanol are shown in Scheme 3. This ter-molecular interaction is supported by the ^{13}C NMR results shown in Figure 8. Figure 14 shows the energy diagram of the catalysis of the urethane formation due to dimethyltin methoxy acetate O-coordinated interaction calculated using water as the medium. Enthalpy and Gibbs free energy differences for TS1 are ΔH_{298} = 54.72 kJ mol^{-1}, ΔG_{298} = 158.91 kJ mol^{-1} ($\Delta H^{\ddagger}$ = 55.07 kJ mol^{-1}, $\Delta G^{\ddagger}$ = 85.94 kJ mol^{-1}), respectively, and for TS2 ΔH_{298} = 43.14 kJ mol^{-1}, ΔG_{298} =153.20 kJ mol^{-1} ($\Delta H^{\ddagger}$ = 5.30 kJ mol^{-1}, $\Delta G^{\ddagger}$ = 9.74 kJ mol^{-1}), respectively. TS1 is the transition state for the formation of organotin carbonimidate and TS2 is the transition state for the conversion of organotin carbonimidate to urethane and DMTMA. The total change in enthalpy and Gibbs free energy with respect to starting material to product is -85.37 and -34.18 kJ mol^{-1}. It can be seen that the activation energy for this reaction is 51.42 kJ mol^{-1}, compared to the reaction catalysed by dimethyltin diacetate, which has an activation energy of 85.18 kJ mol^{-1}. Figure S2 shows the intrinsic reaction coordinate plots for transition states TS1 and TS2 for the interaction energy diagram shown in Figure 14. Both plots show significant curvatures indicating that the forward reaction is probable.
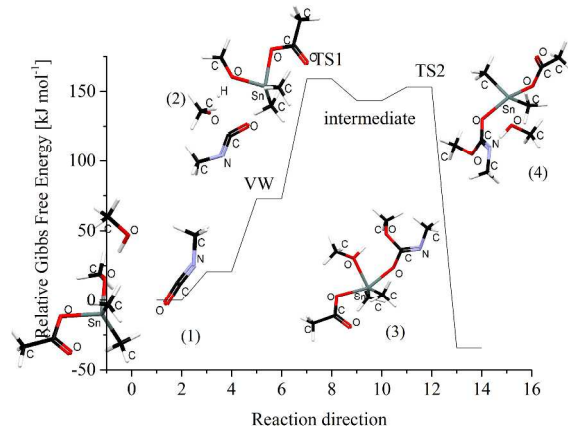
Figure 14. Energy diagram for the reaction between methyl isocyanate and methanol in the presence of DMTMA (O-coordinated interaction) in polar medium.

The higher reaction rate in the polar solvent may be due to the formation of organotin alkoxide. This is further supported by the increased catalytic action observed when reaction product of the mixture of DBTDB + acetic acid (1:1 mole) was used as a catalyst. In this calculation water was used as the medium.
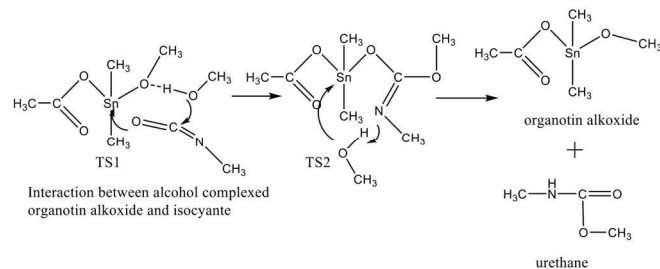
Scheme 3. Organotinalkoxide catalysis of urethane formation with O-coordinated interaction

4.2.2 N-coordinated interaction of the isocyanate

The alkoholated DMTMA allows the possibility of the isocyanate molecule to approach in a N-coordinated fashion, which will lead to the formation of the organotin carbamate. The reaction is shown in scheme 4. As stated in literature, the interaction takes place between the isocyanate carbon and the alkoxy oxygen, resulting in the formation of the tin carbamate. The tin carbamate will further interact with alcohol to regenerate the organotin alkoxide and the urethane. The energy diagram for the interaction is shown in Figure 15. The enthalpy and Gibbs free energy differences for TS1 and for TS2 are $\Delta H_{298} = 37.43$ kJ mol^{-1}, $\Delta G_{298} = 133.96$ ($\Delta H^{\ddagger} = 36.55$ kJ mol^{-1}, $\Delta G^{\ddagger} = 88.12$ kJ mol^{-1}) and $\Delta H_{298} = 10.50$, $\Delta G_{298} = 122.13$ ($\Delta H^{\ddagger} = 59.91$ kJ mol^{-1}, $\Delta G^{\ddagger} = 73.44$ kJ mol^{-1}), respectively. TS1 is the transition sate for the formation of organotin carbamate and TS2 is the transition state for the conversion of organotin carbamate to urethane and DMTMA. The activation energy for the first transition is 27.98 kJ mol^{-1}. The total change in enthalpy and Gibbs free energy with respect to starting material to product is -85.37 and -34.18 kJ mol^{-1}. Figure S3 shows the intrinsic reaction coordinate plots for the transition states TS1 and TS2 in the energy diagram shown in Figure 15. It can be seen that plot for transition state TS2 has a lower curvature indicating a slower forward reaction. When considering intrinsic reaction coordinate data for the second transition TS2 for the O-coordinated and N-coordinated interactions and DMTMA used as the catalyst, it can be seen that the curvature in Figure S3 (bottom) is less than in Figure S2 (bottom), which suggests that the N-coordinated reaction may have a slower overall reaction rate. Figure 16 shows the van der Waals complexes formed from the interaction between alcoholized DMTMA and methyl isocyanate starting from N-coordinated orientation (as shown in Figure 17, left) after energy optimization in non-polar (toluene, Figure 16, left) and polar (water, Figure 16, right) media, respectively. Enthalpies and Gibbs free energies for these two complexes for the O-coordinated complex in toluene and N-coordinated complex in water are $\Delta H_{298} = -14.14$ kJ mol^{-1}, $\Delta G_{298} = 59.10$ kJ mol^{-1} and $\Delta H_{298} = 0.88$ kJ mol^{-1}, $\Delta G_{298} = 45.83$ kJ mol^{-1}, respectively. However, the distance between the interacting molecules is significantly higher for the N-

coordinated assembly (Sn-O 6.65 Å) in polar media as for the O-coordinated interaction (Sn-O 3.21 Å) in non-polar media.
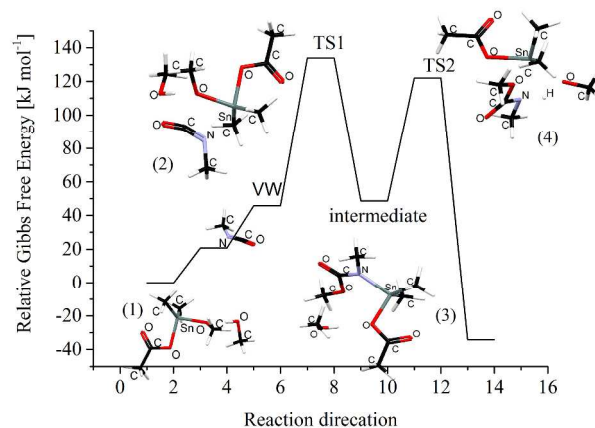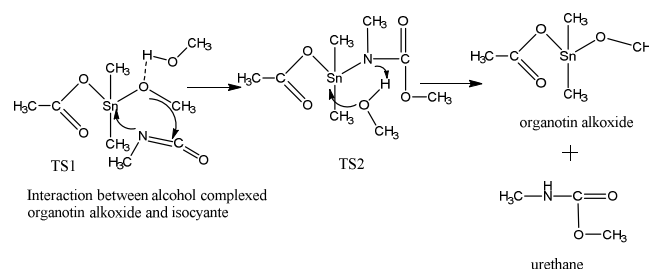

Figure 15. Energy diagram for the reaction between methyl isocyanate and methanol in the presence of DMTMA (N-coordinated interaction) in polar medium.

Scheme 4. Organotin alkoxide catalysis of urethane formation. N-coordinated interaction; the interaction is found between the N of the isocyante and O of the alkoxide.

The large separation of the N-coordinated interaction in polar media indicates the separation of alcohol organotin alkoxide complex and the isocyanate, as only the interaction between the Sn-compound and methanol can be observed. The optimization showed two disjointed cavities. The O-coordinated structure in polar media is shown in Figure 17 (right). The distance between interacting molecules is higher than in non-polar solvents (Sn-O 3.23 Å). Enthalpy and Gibbs free energy of the O-coordinated complex in polar media are $\Delta H_{298} = -0.35$ kJ mol^{-1} and $\Delta G_{298} = 72.96$ kJ mol^{-1}, respectively. Therefore, the O-coordinated approach could be more probable in polar medium, although its activation energy is higher.

As seen from Figure 1, the initial increase in the reaction rate in polar solvents is due to tin alkoxide being formed because of solvent effects. It is also seen from Figure 1 that the reaction rate decreases with depletion of NCO, this is caused by the reduction of the alcohol content in the medium. This will reduce the stability of tin alkoxide (dimerization) that is formed in the reaction mixture, resulting in lack of alcohol to drive the reaction forward. This situation has improved with an increasing alcohol concentration as seen from Figure 3. However, at the end of the reaction the formation of the original catalyst will depend on the availability of the carboxylic acid. The behaviour of the organotin carboxylate in polar media explains the mechanism proposed in literature[9].
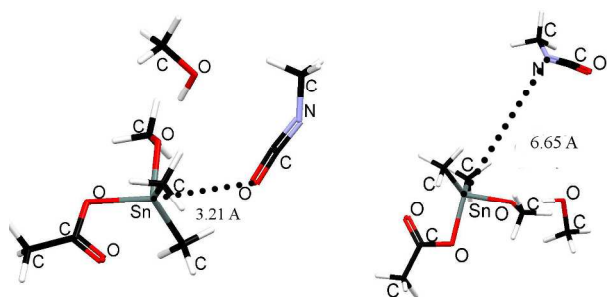
Figure 16. Van der Waals complexes for the interaction between DMTMA, methanol and methyl isocyanate in non-polar medium (O-coordinated, left) and in polar medium (N-coordinated, right).
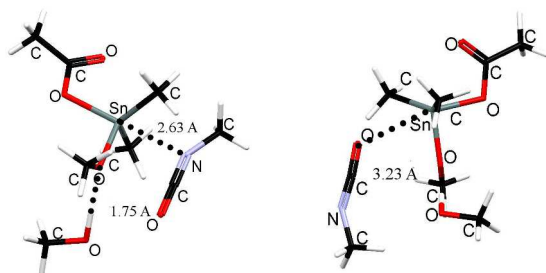

Figure 17. Starting molecular assembly in search for the O-coordinated and N-coordinated van der Waals complexes in polar and non-polar medium(left) and O-coordinated van der Waals complex in polar medium (right).

From the above discussion it is evident that for the preparation of aliphatic pre-polymers and by using organotin carboxylate catalyst, the catalyst can convert to its alkoxide. As shown in section 3.1.2, the alkoxide formed can affect the stability of the pre-polymer during storage.

4.3 Aromatic isocyanate

It has previously been shown that for organotin carboxylate catalysis of aromatic isocyanate the reaction rate is independent of the number of carboxylate ligand associated with the organotin carboxylate[24]. It was found that organotin alkoxide has the same reaction rate as the organotin carboxylate catalyst in urethane formation for aromatic isocyanate. From these results it was confirmed that in non-polar solvents the dominant catalyst for an aromatic system is the organotin alkoxide. This work shows that the aromatic isocyanate and alcohol interact with organotin di carboxylate catalyst similar to the reaction shown in Scheme 2 (the first step). This mechanism leads to the formation of the organotin alkoxide. However, in both polar and non-polar systems the interaction between DMTDA, methyl alcohol and phenyl isocyanate lead to the formation of an intermediate similar to as shown in Figure 18. In this intermediate, the proton of the carboxylic acid that is attached to the tin centre is on the opposite side to the nitrogen of the carbonimide group. This makes the nitrogen of the carbonimide group to interact with the proton of the OH group of the alcohol molecule to form a urethane and the organotin alkoxide. It can also be shown that for organotin alkoxide the activation energies for the catalysis of aromatic

isocyanates in urethane formation is higher in polar solvents compared to non-polar solvents. This means the reactivity in polar solvents will be slower compared to non-polar solvents, as seen in Figure 6. Reaction rate studies show that the reaction rate of organotin carboxylate catalysed aromatic isocyanate is independent of the carboxylate ligand content in polar solvent as seen from Figure 6. Therefore it is possible to say that in polar solvent the dominant catalyst is the organotin alkoxide similar to non-polar solvent. Organotin alkoxides exist at least in a dimerized form[36]. Enthalpies and Gibbs free energies for dimerized DMTDM in toluene and water are ΔH_{298} = -50.98 kJ mol^{-1}, ΔG_{298} = 15.61 kJ mol^{-1} and ΔH_{298} = -42.40 kJ mol^{-1}, ΔG_{298} = 22.66 kJ mol^{-1}, respectively. This suggests that in the polar solvent DMTDM can exist as monomer compared to non-polar solvents.
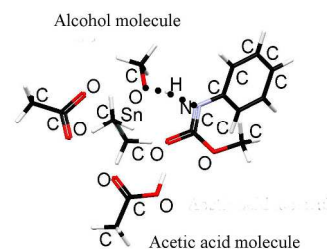

Figure 18. Intermediate formed in the DMTDA catalysis of the phenyl isocyanate in urethane formation. (DFT / B3LYP LAND2DZ / 6-31G*).

DMTDM can interact with two molecules of methanol to give an alcoholysis product. In polar medium, its enthalpy and Gibbs free energy are ΔH_{298} = -26.65 kJ mol^{-1} and ΔG_{298} = 41.93 kJ mol^{-1}, respectively. Simulations show that alcoholysed DMTDM interact with phenyl isocyanate to give an O-coordinated interaction. The alcoholised dimerized form of the organotin alkoxide shows a lower probability of forming N-coordinated complexes due to steric effects. Therefore, an aromatic system is catalysed through an O-coordinated van der Waals complex; the optimised structure is shown in Figure 19. The van der Waals complexes have enthalpies and Gibbs free energies calculated from starting material ΔH_{298} = -52.02 kJ mol^{-1}, ΔG_{298} =82,14 kJ mol^{-1} and $\Delta H_{298 =}$ -33.17 kJ mol^{-1}, ΔG_{298} = 98.49 kJ mol^{-1} in toluene and water, respectively, leading to a ter-molecular interaction as seen in our previous publication[24]. The ^{13}C NMR data shown Figure 9 support this modelling result.
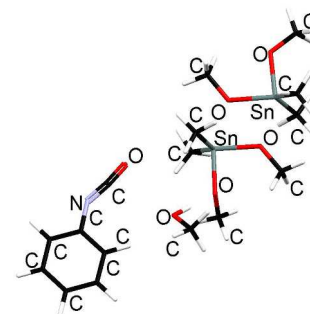

Figure 19. Optimized geometry of the dimerized organotin alkoxide, phenyl isocyante and methanol ter-molecular assembly (toluene was used as the medium).

5 Conclusion

The catalytic action of organotin carboxylate in polar solvents shows a higher rate compared to non-polar medium for primary aliphatic systems. The reason for the increase in reactivity is due to the formation of tin alkoxide, which acts as a catalyst. This is similar to what is proposed in literature[2]. In the case of the aromatic isocyanate, the catalysis is due to the formation of organotin alkoxide resulting in one single type of mechanism in both polar and nonpolar media. This will lead to higher activation energy in the polar medium to give an overall lower reaction rate. The catalysis takes place through an O-coordinated configuration predominantly for both aromatic and aliphatic isocyanates when dibutyltin carboxylate catalyst is used in polar solvents.

Acknowledgement

Notes

[a] School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland, New Zealand.

[b] Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University Auckland, New Zealand; E-mail: t.soehnel@auckland.ac.nz; Tel: 0064 9 373 7599 ext 89722

References

† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

(1)   Bloodworth, A. J.; Davies, A. G. *Journal of the Chemical Society (Resumed)* **1965**, 5238.

(2)   Houghton, R. P.; Mulvaney, A. W. *Journal of Organometallic Chemistry* **1996**, *518*, 21.

(3)   Houghton, R. P.; Mulvaney, A. W. *Journal of Organometallic Chemistry* **1996**, *517*, 107.

(4)   Bacaloglu, R.; Cotarcâ, L.; Marcu, N.; Tölgyi, S. *Journal für Praktische Chemie* **1988**, *330*, 541.

(5)   Van Der Weij, F. W. *Journal of Polymer Science: Polymer Chemistry Edition* **1981**, *19*, 381.

(6)   van der Weij, F. W. *Journal of polymer science. Part A-1, Polymer chemistry* **1981**, *19*, 3063.

(7)   Draye, A. C.; Tondeur, J. J. *Journal of Molecular Catalysis A: Chemical* **1999**, *138*, 135.

(8)   Draye, A. C.; Tondeur, J. J. *Journal of Molecular Catalysis A: Chemical* **1999**, *140*, 31.

(9)   Gielen, M.; Davies, A. G.; Pannell, K.; Tiekink, E. *Tin Chemistry: Fundamentals, Frontiers, and Applications*; Wiley, 2008.

(10)   Reegen, S. L.; Frisch, K. C. *Journal of Polymer Science Part A-1: Polymer Chemistry* **1970**, *8*, 2883.

(11)   Szycher, M. *Szycher's Handbook of Polyurethanes, First Edition*; Taylor & Francis, 1999.

(12)   Bock, M. *Polyuretahne Coatings*; Vinzent, 2001.

(13)   Randall, D.; Lee, S. *The polyurethanes book*; Distributed by J. Wiley, 2002.

(14)   Raspoet, G.; Nguyen, M. T.; McGarraghy, M.; Hegarty, A. F. *Journal of Organic Chemistry* **1998**, *63*, 6878.

(15)   Samuilov, A. Y.; Zenitova, L. A.; Samuilov, Y. D.; Konovalov, A. I. *Russian Journal of Organic Chemistry* **2008**, *44*, 1316.

(16)   Samuilov, A. Y.; Zenitova, L. A.; Samuilov, Y. D.; Konovalov, A. I. *Russian Journal of Organic Chemistry* **2009**, *45*, 68.

(17)   Samuilov, A. Y.; Balabanova, F. B.; Kamalov, T. A.; Samuilov, Y. D.; Konovalov, A. I. *Russian Journal of Organic Chemistry* **2010**, *46*, 1452.

(18)   Hatanaka, M. *Bulletin of the Chemical Society of Japan* **2009**, *82*, 1149.

(19)   Çoban, M.; Konuklar, F. A. S. *Computational and Theoretical Chemistry* **2011**, *963*, 168.

(20)   Malwitz, N. *Journal of Physical Chemistry* **1995**, *99*, 5291.

(21)   Malwitz, N. *CAChe connection*; 1 ed.; CAChe scientific, P.O. Box 500, MS 13-400, Beaverton, OR., 1992.

(22)   Hatanaka, M. *Bulletin of the Chemical Society of Japan* **2011**, *84*, 933.

(23)   Devendra, R.; Edmonds, N. R.; Söhnel, T. *Journal of Molecular Catalysis A: Chemical* **2014**, *395*, 72.

(24)   Devendra, R.; Edmonds, N. R.; Söhnel, T. *Journal of Molecular Catalysis A: Chemical* **2013**, *366*, 126.

(25)   Foresman, J. B.; Frisch, A. E.; Gaussian, I. *Exploring chemistry with electronic structure methods*; Gaussian, Inc., 1996.

(26)   Kraka, E.; Cremer, D. *Accounts of Chemical Research* **2010**, *43*, 591.

(27)   M.J. Frisch, G. W. T., H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Gaussian, Inc.: Wallingford CT, 2009. 2013.

(28)   Spartan'10 Wavefunction Inc. Irive, C. W. J. H., A Guide to Molecular Mechanics and Quantum Chemical Calculations, Wavefunction, Inc., Irvine, CA,; Y. Shao, L.F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S.T. Brown, A.T.B. Gilbert, L.V. Slipchenko,

S.V. Levchenko, D.P. O'Neill, R.A. DiStasio Jr., R.C. Lochan, T. Wang, G.J.O. Beran, N.A. Besley, J.M. Herbert, C.Y. Lin, T. Van Voorhis, S.H. Chien, A. Sodt, R.P. Steele, V.A. Rassolov, P.E. Maslen, P.P. Korambath, R.D. Adamson, B. Austin, J. Baker, E.F.C. Byrd, H. Dachsel, R.J. Doerksen, A. Dreuw, B.D. Dunietz, A.D. Dutoi, T.R. Furlani, S.R. Gwaltney, A. Heyden, S. Hirata, C-P. Hsu, G. Kedziora, R.Z. Khalliulin, P. Klunzinger, A.M. Lee, M.S. Lee, W.Z. Liang, I. Lotan, N. Nair, B. Peters, E.I. Proynov, P.A. Pieniazek, Y.M. Rhee, J. Ritchie, E. Rosta, C.D. Sherrill, A.C. 2013.

(29)   Anderson, M. J.; Whitcomb, P. J. *DOE Simplified: Practical Tools for Effective Experimentation*; Taylor & Francis, 2000.

(30)   Design-Expert www.statease.com, 2013.

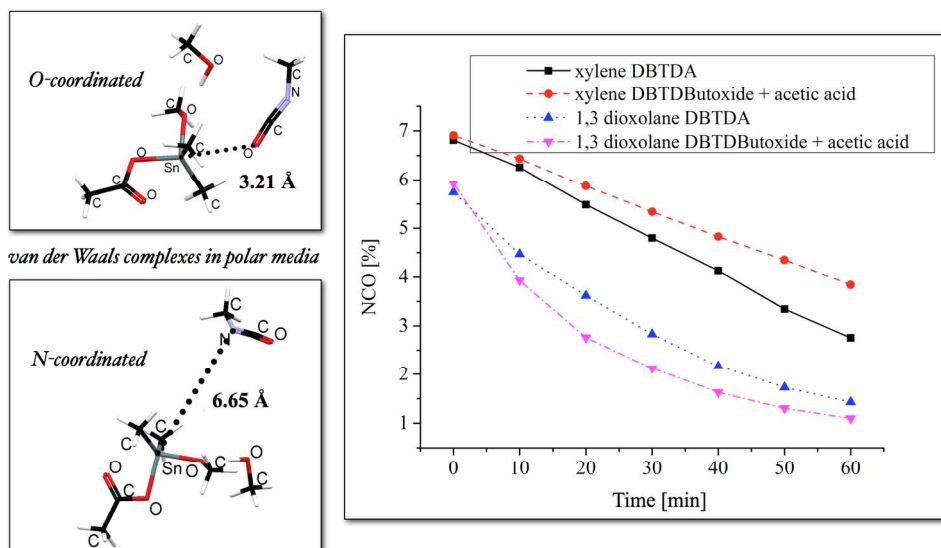(31)   ASTM-D2572-97; ASTM International: West Conshohocken, Pennsylvania 19428., 1997.

(32)   Davies, A. G.; Harrison, P. G. *Journal of the Chemical Society C: Organic Chemistry* **1967**, 298.

(33)   Hatada, K.; Ute, K.; Oka, K.-I. *Journal of Polymer Science, Part A: Polymer Chemistry* **1990**, *28*, 3019.

(34)   Zhao, Y.; Truhlar, D. G. *Theoretical Chemistry Accounts* **2008**, *120*, 215.

(35)   Adams, M. R.; Bushnell, E. A. C.; Bruce Grindley, T.; Boyd, R. J. *Computational and Theoretical Chemistry* **2014**, *1050*, 7.

(36)   Wakamatsu, K.; Orita, A.; Otera, J. *Organometallics* **2010**, *29*, 1290.

677x381mm (72 x 72 DPI)