Journal of Molecular Catalysis A: Chemical 395 (2014) 72–86

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

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

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

[a] *School of Chemical Sciences, The University of Auckland, New Zealand*
[b] *Centre for Theoretical Chemistry and Physics, The New Zealand Institute for Advanced Study, Massey University, Auckland, New Zealand*

ARTICLE INFO

Article history:
Received 6 May 2014
Received in revised form 16 July 2014
Accepted 2 August 2014
Available online 12 August 2014

Keywords:
Organotin compounds
Urethane formation
Catalyst
Isocyanate
Computational

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.

1. Introduction

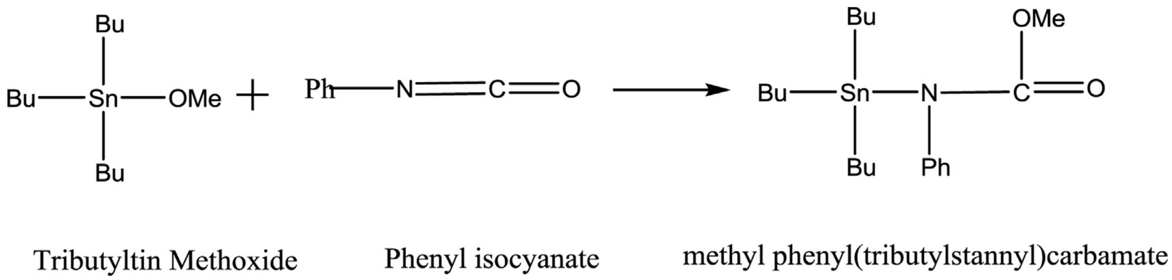
Polyurethanes are formed by the reaction between a polyisocyanate and a polyol. They are major groups of polymers used in products such as coatings, adhesives, elastomers and composites [2]. However, as in most chemical reactions, catalysts are used in practical applications of polyurethane synthesis. 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

---

* Corresponding author at: School of Chemical Sciences, The University of Auckland, New Zealand. Tel.: +64 9 923 9722; fax: +64 9 373 7422.
E-mail address: t.soehnel@auckland.ac.nz (T. Söhnel).

http://dx.doi.org/10.1016/j.molcata.2014.08.003
1381-1169/



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

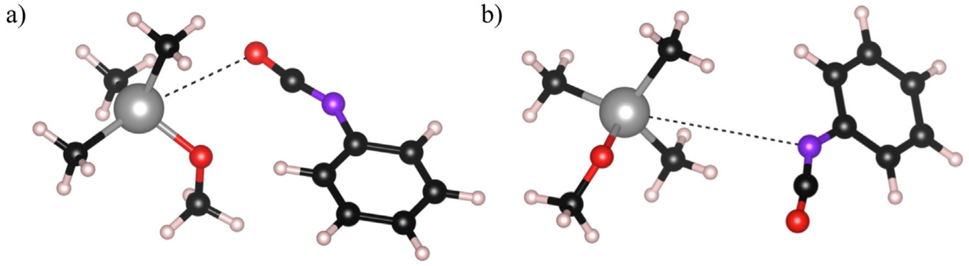
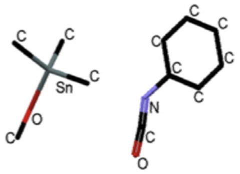
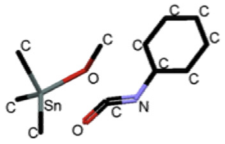
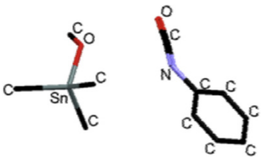
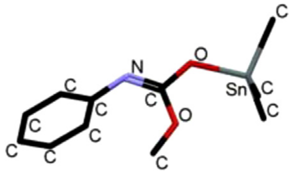
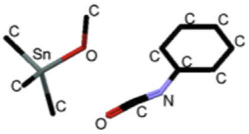


Fig. 1. Starting configuration of the interaction between trimethyltin methoxide with phenylisocyanate (a) oxygen of the isocyanate is positioned closed to tin center; (b) nitrogen of the isocyanate is positioned closed to the tin center.

Table 1
Molecular structures associated with energy profile of interaction between trimethyltin methoxide and phenyl isocyanate.

Index	Structure	Index	Structure
1		4	
2		5	
3			

optimizing the energy of a system with trimethyltin methoxide and phenyl isocyanate with the N atom positioned towards Sn without constrains (Fig. 1(b)), the system rearranges such that the oxygen of the isocyanate is directed towards the tin atom of the trimethyltin methoxide molecule (Fig. 1(a)). Fig. S1 shows the electrostatic isopotential surface for trimethyltin methoxide and phenyl isocyanate. It can be seen that when the nitrogen of the phenyl isocyanate is placed in the direction of N-coordination with the tin atom the interaction of the electrostatic fields seem to prevent such interaction. This could explain the reason for the rearrangement to an O-coordination of the phenyl isocyanate with the tin atom. However, high-energy complexes between trimethyltin methoxide and phenyl isocyanate with the nitrogen of the isocyanate group being directed towards the tin atom will be discussed in subsequent section.

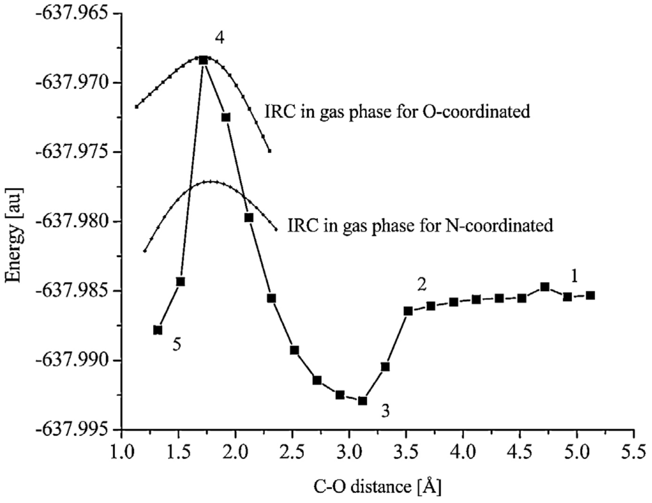


Fig. 2. Energy profile for the interaction between trimethyltin methoxide and phenyl isocyanate with initial configaration where nitrogen of the isocyanate is close to the tin atom.

The same simulation was carried out using CPCM models for the non-polar and polar solvents toluene and water. Both simulations also showed that the initial N-coordination changed to an O-coordination. This indicates that the interaction between trimethyltin methoxide and phenyl isocyanate is most probably realized via the oxygen of the isocyanate. Information related to the reaction path for the N-coordinated interaction was obtained from IRC data starting from the Sn–N transition state, which was obtained by a trial and error method as mentioned previously and also a van der Waals complex. However, we were not able to simulate the interaction starting from the van der Waals complex in gas phase since the orientation change again to the O-coordination. Fig. 2 shows the gas phase IRC plot for the two interactions. These plots are done in a different scale for clarity.

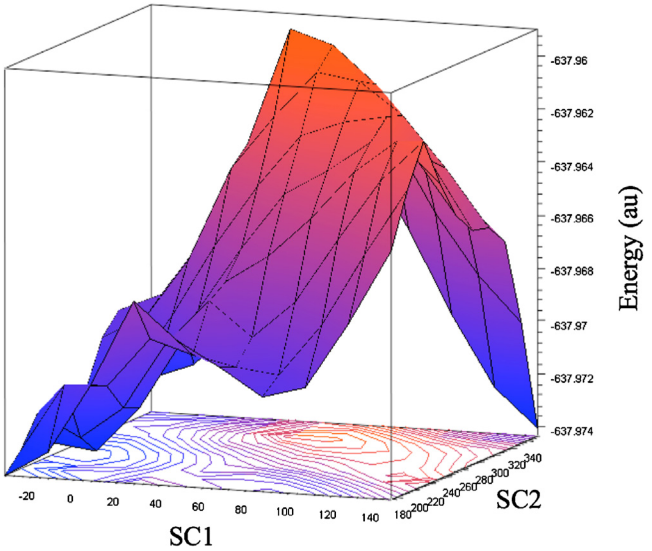


Fig. 3. Potential energy surface for the rotation of the phenyl isocyanate molecule from O-coodinated to N-coordinated orientation in gas phase.

Structure 1 (Table 1) as the initial orientation of the two molecules has a distance of 5.12 Å between the alkoxy oxygen and isocyanate carbon. In structure 2 the distance between the same atoms is reduced to 3.52 Å. Fig. S2a shows the electrostatic isopotential surface for structure 2. It can be seen that the electrostatic fields of the two oxygen atoms are interacting. At this distance the isocyanate molecule tends to rotate to adopt the new orientation of structure 3 (O-coordination). The reason may be due to the interaction between the electrostatic fields as explained in the previously. Fig. S2b shows the electrostatic isopotential surface for structure 3. The interaction between electrostatic fields around individual atoms is now less than in structure 2. This can be further explained as the Lewis action between the organotin center and the isocyanate oxygen. Finally, the insertion reaction takes place with the movement of the alkoxy group of the organotin and latching on to the positive charged isocyanate carbon. Structure 4 represents the transition state for the insertion reaction. The distance between the isocyanate carbon and alkoxy oxygen is 1.71 Å. With the insertion reaction the isocyanate oxygen gets bonded on to the tin center to form an organotin O-substituted carbamate (methyl tributylstannyl phenylcarbonimidate). From this point further steps will take place as explained in the subsequent sections. We have also simulated the rotational barrier between the two reaction pathways. Fig. 3 shows the potential energy surface for the rotation of the phenyl isocyanate molecule from O-coordination to N-coordinate orientation. The barrier was calculated for the molecular assembly, where the distance between the C—O of the O-coordinated interaction was set to a pre-selected value to change to the N-coordinated orientation. The pre-selected distance of 1.97 Å was taken as the distance between the C—O for transition state of N-coordinated interaction, which is approximately the distance between isocyanate carbon and the alkoxide oxygen at N-coordinated transition state. At this distance rotational barrier is 32.1 kJ mol^{-1} for the O-coordinated interaction to rearrange to N-coordinated interaction. This is also about 16.3 kJ mol^{-1} higher than the O-coordinated transition state. This data suggest that the O-coordination has a rotational energy barrier, which prevents it from entering to the N-coordinated reaction pathway.

3.2. Energy diagrams for the two pathways

Fig. 4 shows the energy diagram for the two types of interactions that were discussed previously. Pathway 1 lead to the formation of N-substituted phenyl carbamate (methyl phenyl(trimethylstannyl) carbamate) and pathway 2 leads to the formation of O-substituted phenyl carbamate (methyl trimethylstannyl phenylcarbonimidate), which subsequently rearrange to N-substituted phenyl carbamate (methyl phenyl(trimethylstannyl)carbamate). The activation energy for the first transition state for pathway 1 is 23.9 kJ mol^{-1} less than for pathway 2.

From Fig. 4 it can be seen that pathway 1 has two transition states and for pathway 2 three transition states can be found. For pathway 1 TS11 (95.5 kJ mol^{-1}) in the interaction between trimethyl tin methoxide and phenyl isocyanate form the trimethyl tin N-phenyl carbamate (methyl phenyl(trimethylstannyl)carbamate), where the oxygen of the methoxy group is coordinated with tin atom. TS12 (79.8 kJ mol^{-1}) represents the rotation of the isocyanate carbonyl to form the trimethyl tin N-phenyl carbamate. In pathway 2 TS21 (132.9 kJ mol^{-1}) is to form trimethyl tin O-phenyl carbamate (methyl trimethylstannyl phenyl carbonimidate). For pathway 2, TS22 (90.1 kJ mol^{-1}) corresponds to the rearrangement of the carbamate to give N-coordinated species by rotating around the Sn—O—C—N dihedral angle, whereas TS23 (42.68 kJ mol^{-1}) is the transition state for the change from O-substituted (methyl trimethylstannyl phenylcarbonimidate) to N-substituted (methyl phenyl(trimethylstannyl)carbamate) carbamate. This leads to the formation of the N-substituted phenyl carbamate (methyl phenyl(trimethylstannyl)carbamate) as given in literature [1]. The value in the bracket is the free energy difference from the starting material at 298 K in gas phase.

The free energy is an indication of the conversion of reactants to products. It is interesting to see that the free energy difference between the starting materials trimethyltin methoxide and phenyl isocyanate and the final product trimethyltin N-phenyl carbamate is positive, which indicate that the reactants are more stable than the product. In our calculation we used DFT (B3LYP and PBE) and *ab initio* MP2 with various basis sets such as 6-31G*, 6-31+G** and DGDZVP for light elements. DFT-B3LYP and MP2 using 6-31G* basis set resulted in positive Free energies 12.51 and 6.79 kJ mol^{-1}, respectively; the DFT-BPE functional gave values 0.69 kJ mol^{-1} using 6-31G* basis set which was close to zero. However, with DFT/B3LYP using DGDZVP basis sets a negative value of −2.33 kJ mol^{-1}was obtained. Steps were also taken to calculate the free energy difference between triethyltin methoxide and phenyl isocyanate and the reaction product triethyltin-N-phenyl carbamate, which gave a positive value of 18.39 kJ mol^{-1} as well using DFT B3LYP level of theory with 6-31G* basis set. However, the product formation from reacting TBTM and phenyl isocyanate seems to be more stable than the information from thermochemical data from model compounds. ^{13}C NMR and FTIR measurements indicate that the reaction between TBTM and phenyl isocyanate (1:1 mole) leads to the formation of tributyltin phenyl carbamate without any residual phenyl isocyanate. This may be due to the stabilization of the product due to hydrogen bonding from urethane formed because of methanol being present as an impurity. If phenyl isocyanate is replaced with methyl isocyanate the reaction product with TMTM gives a negative free energy difference −8.78 kJ mol^{-1} using DFT B3LYP with 6-31G* basis set. The free energy difference for the reaction was also calculated using the optimized geometries obtained from DFT B3LYP LANL2DZ/6-31G* level of theory with DFT B3LYP and PBE with LANL2DZ/6-311+G(2df,2p) level of theory using single point gave 12.5 and −9.1 kJ mol^{-1}. The calculations do not result in a uniform picture as the free energy has sometimes a positive and sometimes a negative value. Experimentally, the

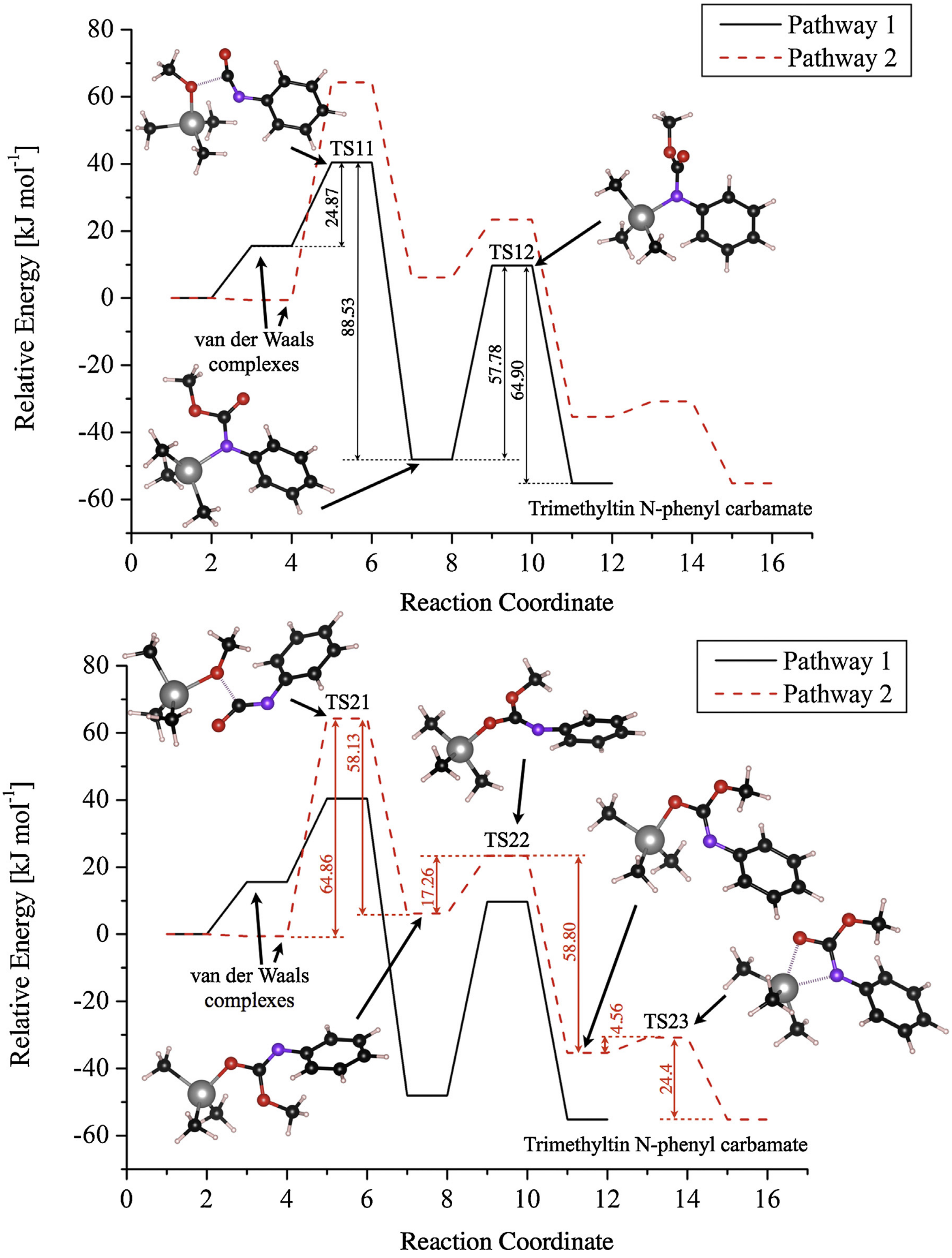


Fig. 4. Energy diagram for the interaction between trimethy tin methoxide and phenyl isocyanate: top: energie values, intermediate structures and transitions states for pathway 1 are shown; bottom: energie values, intermediate structures and transitions states for pathway 2 are shown; the energy profile of both pathways are shown in both figures.

reaction between TBTM and phenyl isocyanate results in the formation of tributyltin phenyl carbamate. Therefore, we should assume that the free energy difference for model reaction results in a negative value. Overall, the simulations of the interaction between trialkyltin alkoxide and phenyl isocyanate indicate that the initial interaction is realized between isocyanate oxygen and the tin center. During this processes the alkoxide group attached to the tin center is transferred onto the isocyanate carbon. However, with the bond rotation about the C—O bond the carbonyl group will rearrange to form the N—Sn bond to give the tin carbamate as reported by Bloodworth and Davies as shown in Fig. 4. Calculations also showed that aliphatic isocyanates lead to the formation

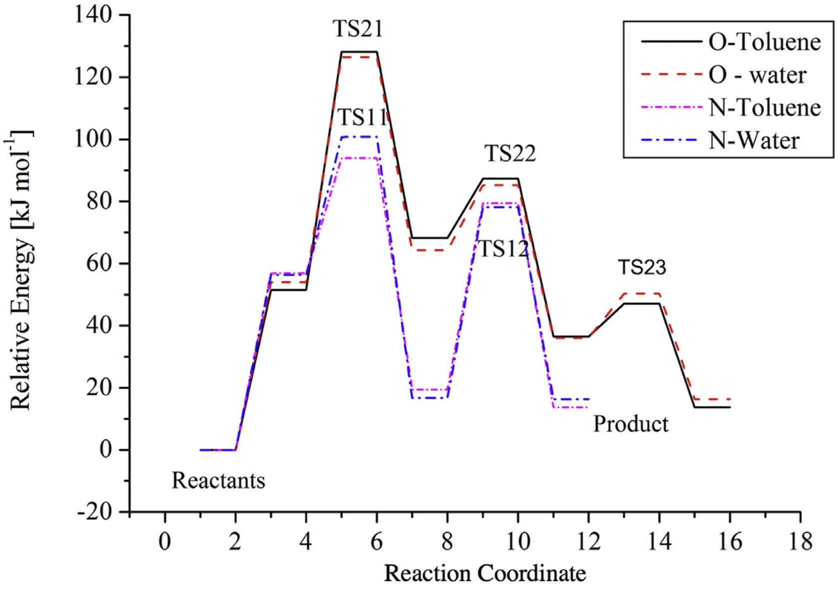


Fig. 5. Free energy difference for the two reaction path in toluene and water media.

of N—Sn bonds much easier than aromatic isocyanate form a O-substituted carbamate (methyl trimethylstannyl methylcarbonimidate) due to the low activation energy. The activation energies for aliphatic and aromatic systems from corresponding minima of O-substituted carbamate (methyl tributylstannyl carbonimidate) are 2.1 and 4.6 kJ mol^{-1}, respectively. The reason may be due to a higher nucleophilicity of the nitrogen atom of the aliphatic stannyl carbonimidate in comparison to the N atom of the aromatic stannyl carbonimidate. However, in an alcohol rich environment the reaction may not take place through this route due to hydrogen bonding of the alcohol with the nitrogen of the stannyl carbonimidate.

All transition states were optimized in the gas phase as discussed before as well as in solution with water as polar as well as toluene as non-polar medium. The activation free energy was calculated at 298 K as the difference in energy between the transition state and the reactants. Fig. 5 shows the free energy plot for the two pathways in toluene and water. It can be seen that in case of the N-coordinated pathway, the polar media will retard the reaction due to the higher activation free energy in polar medium whereas the O-coordinated pathway will not show much different between polar and non-polar media. It is also interesting to see that in both media the final free energy is higher than the starting material, as observed in the gas phase. We also calculated the free energy differences for the reactions in toluene and water using the DFT PBE functional. The geometry of the reaction product trimethyltin phenyl carbamate had converging problems when water was used as solvent. However, by using toluene as solvent, the free energy difference gave positive value close to zero.

These energies were calculated by assuming that all transition states and van der Waals complexes are formed in the reaction mechanism. If such starting van der Waals complexes exist then pathway 1 is the most probable reaction mechanism. However, this will depend on the possibility of formation of appropriate van der Waals complexes when the molecules are approaching each other from larger distances. The formation of the van der Waals complexes in this mechanism is discussed next.

3.3. van der Waals complexes for the two different pathways

We were able to establish van der Waals complexes for two different pathways using IRC techniques following the path for each transition state. It turned out to be the only method that could be used to find a stable van der Waals complex for the N-coordinated configuration. The level of theory used in this calculation was DFT B3LYP/LANL2DZ/6-31G*. Tables S1 and S2 show the X, Y, Z coordination for each atom in the complexes for O- and N-coordinated van der Waals complexes as seen in Fig. 6.

The van der Waals complexes observed in the system are important for the determination of the correct reaction mechanism. If the two molecules come in contact and form a stable complex then the chances of these two molecules to undergo a reaction is high. However, in the complex formation their orientation is particularly important. The complex with the lowest energy will be formed predominantly. However, we have noted that the stability of each complex depends on which direction they approach and how the complex is formed initially. In the reaction between TMTM and phenyl isocyanate the N-coordinated van der Waals complex can only be stabilized starting from the N-coordinated transition state, as it is possible to form the O-coordinated van der Waals complex from the O-coordinated transition state. However, the stability also depends on the basis set used in the calculations. Larger basis sets

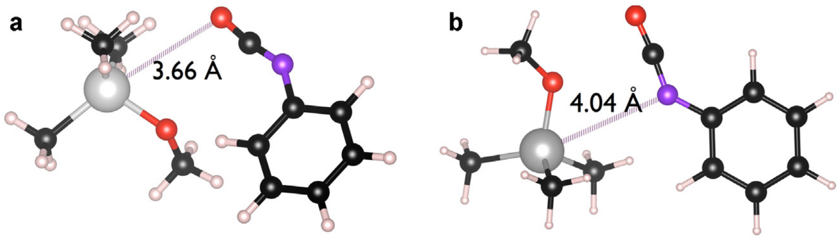


Fig. 6. O-coordinated van der Waals complex (left) and N-coordinated van der Waals complex (right).

Table 2
Thermochemical data for both van der Waals complexes.

Basis set	Media	N-coordinated			O-coordinated		
		ΔH_{298}	ΔG_{298}	ΔZP_0	ΔH_{298}	ΔG_{298}	ΔZP_0
6-31G*	Water	23.31	53.64	19.88	15.53	54.02	12.57
	Toluene	22.83	56.87	19.55	11.22	51.46	8.44
	Gas	20.93	56.91	17.95	5.58	47.71	3.02
6-31+G**	Water	25.35	49.97	21.55	22.44	55.55	19.03
	Toluene	25.56	51.48	21.45	17.58	52.46	14.30
	Gas	–	–	–	10.95	49.73	8.15

All energies are relative and are given in (kJ mol^{-1}).

resulted in converging problems due to weaker interacting forcers within the N-coordinated complex.

Table 2 shows the thermochemical data of the van der Waals complexes formed in the simulation by using different basis sets. It can be seen that with the slightly larger 6-31+G** basis set the N-coordinated complex could not be optimized as a stable solution in the gas phase. Fig. 7 shows the simulations done in the non-polar and polar solvents toluene and water, respectively.

The approach to form the van der Waals complexes directly by bringing the molecules together from larger distances always resulted in the stabilization of the O-coordinated von der Waals complex, even if the initial orientation is N-coordinated (Fig. 7). This effect is very prominent in toluene as non-polar solvent and lees prominent in water as a polar media, but still observable. As mentioned above, the N-coordinated van der Waals complex can only be formed by starting from the N-coordinated transition state. As described earlier, at shorter distances of about 2 Å around the transition state, a rotation barrier of 32 kJ mol^{-1} prevents the molecule to achieve the N-coordinated configuration (gas phase calculation).

The rotational barrier is higher in energy than the O-coordinated transition state by about 16 kJ mol^{-1}, resulting in a preference of the O-coordinated reaction pathway. Therefore, in an interacting situation, where the molecules are approaching from larger distances, the O-coordinated situation is always the predominant coordination.

3.4. Reactivity using intrinsic reaction coordinate plots

We also carried out transition state optimizations for both mechanisms at DFT B3LYP/6-31 + G** level of theory for the light elements and LANL2DZ as basis set for tin the atom and with the CPCM solvent model for toluene and water as non-polar and polar solvents. Fig. 8 shows the IRC plot for both formations of O-(methyl trimethylstannyl phenylcarbonimidate) and N-(methyl phenyl(trimethylstannyl)carbamate) substituted phenyl carbamate. It can be seen that for the O-substituted phenyl carbamate (methyl trimethylstannyl phenylcarbonimidate) the activation potential energy is higher for the non-polar media. However, it is also clear that for the formation of O-substituted phenyl carbamate (methyl phenyl(trimethylstannyl)carbamate) the gradient for non-polar media is higher than in polar media. A lack of curvature in the IRC will retard the reaction to go forward [33,34]. This may offset the reactivity observed in polar media indicating to have a lower reactivity compared to non-polar media.

IRC data for N-substituted phenyl carbamate (methyl phenyl(trimethylstannyl)carbamate) in polar media show a higher activation potential energy than in non-polar media. Both curves show similar gradients after the peak energy, which allows the reactivity in both solvents to be mainly sensitive to the activation energy.

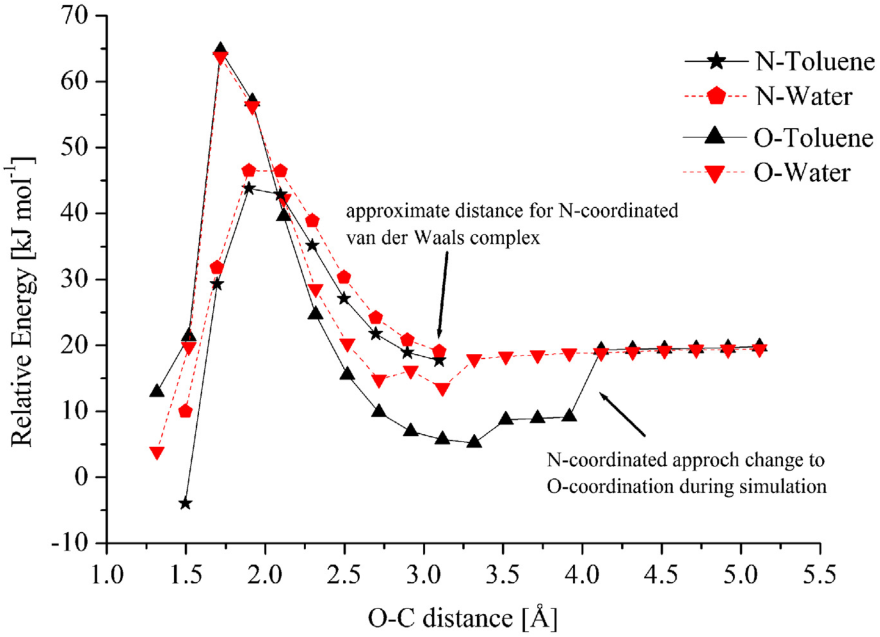


Fig. 7. Energy profile for the interaction between TMTM and phenyl isocyanate starting at N-coordinated configuration in different solvents.

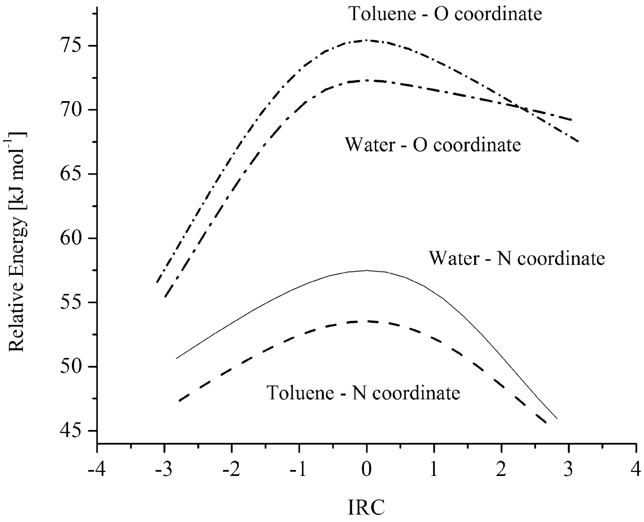


Fig. 8. IRC data for O-coordinated and N-coordinated transition states.

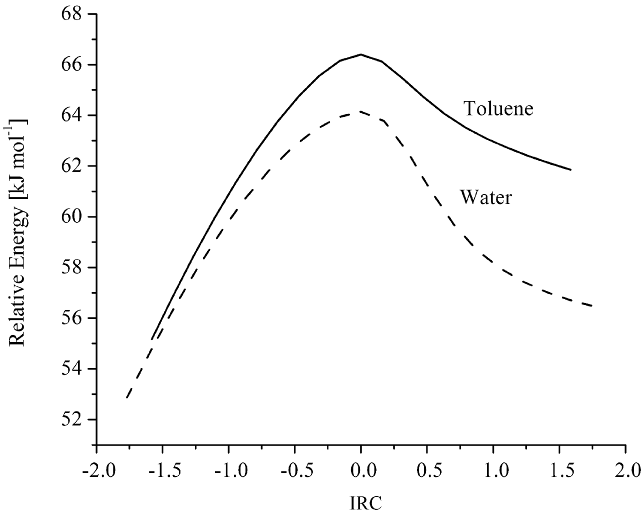


Fig. 10. IRC data for the ternary complex of trimethytin methoxide, methanol and phenyl isocyanate in water and toluene media.

Both reaction pathways give theoretical evidence to have similar reactivities in different solvent environments. However it is difficult to determine which pathway is more likely using an experiment where NCO depletion monitoring during reaction between trialkyltin alkoxide and phenyl isocyanate. As a theoretical example, we have reinvestigated how phenyl isocyanate would react with methanol using trimethyltin methoxide as a catalyst. In this reaction we assume that the catalyst first associates with the alcohol to form a complex, which subsequently interacts with a phenyl isocyanate to form a ternary complex as seen in Fig. 9. The ternary complex shows an enthalpy and free energy of −27.5 and 52.6 kJ mol^{-1} at 298 K, respectively, calculated at the B3LYP LANL2DZ/6-31G* level of theory. The high negative enthalpy indicates the formation of this complex in the mixture. Fig. 10 shows the IRC calculated for transition state for this reaction is both polar and non-polar media using DFT/B3LYP LANL2DZ/6-31+G** level of theory. From the figure it can be seen that the activation energy for the reaction in polar media is less than in non-polar media indicating a higher reaction rate in polar solvents.

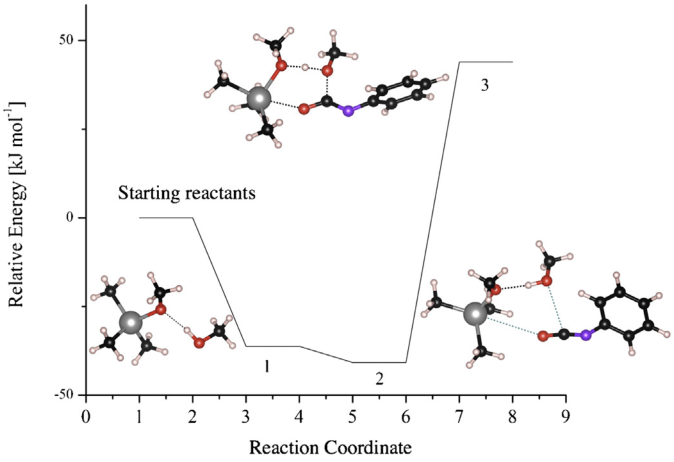


Fig. 9. Interaction between trimethyltin methoxide, methanol and phenyl isocyanate in the formation of the ternary complex.

3.5. Reaction between aromatic isocyanate and alcohol in different solvents in the presence of tributyltin methoxide as catalyst

Fig. 11 shows the depletion of the isocyanate content with time for the reaction between aromatic isocyanate Desmodur 44 V 20 L with 1-butanol in stoichiometric amounts using xylene and THF as non-polar and polar solvents and by using tributyltin methoxide as catalyst. The reaction was carried out as stated in a previous publication by using TBTM as the catalyst in a constant volume [24]. We used a higher amount of catalyst (0.072 g Sn) due to its low catalytic effect. We selected Desmodur 44 V 20 L as the aromatic isocyanate because the reaction product between Desmodur 44 V 20 L and 1-butanol is soluble in xylene and THF by comparing the gradient of the two plots. It can be seen that the reaction in polar media is faster than that of non-polar media. This result shows a similar

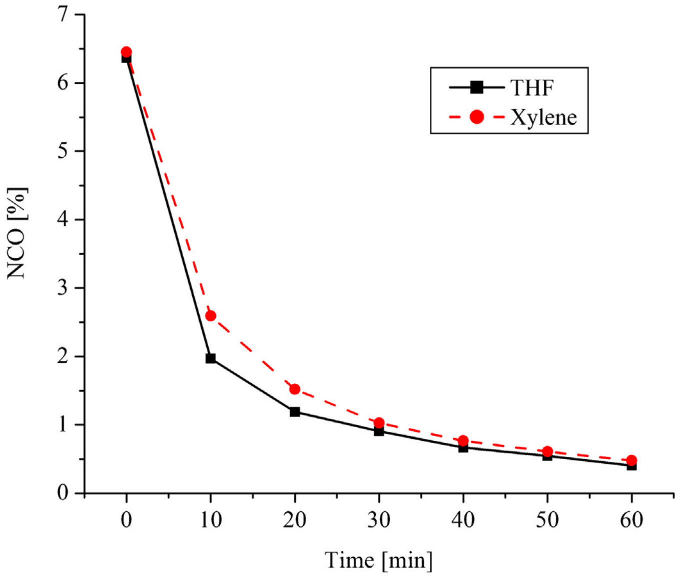


Fig. 11. Depletion of the NCO content in the reaction between Desmodur 44 V 20 L and *n*-butanol at stoichiometric amounts using TBTM (tin content 0.072 g) as a catalyst in xylene and THF.

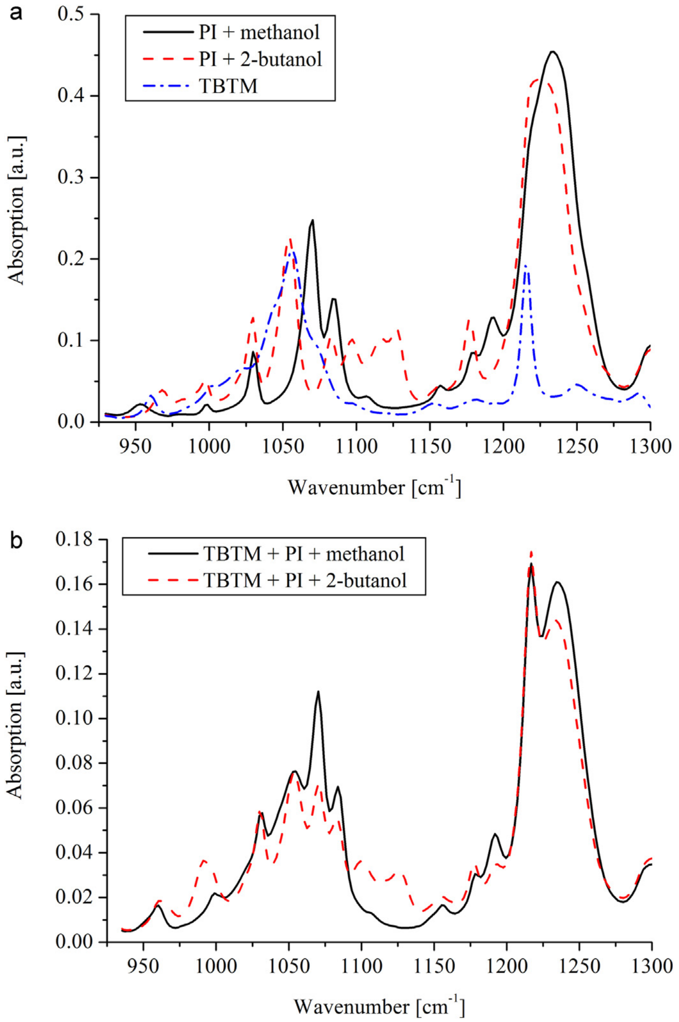


Fig. 12. (a) FTIR/ATR absorption spectra for reaction product of PI + 2-butanol, PI + methanol and TBTM. (b) FTIR/ATR spectra of the two reaction products of TBTM/Phenyl isocyanate with methanol and 2-butanol.

Table 3
FTIR/ATR absorptions in the region 1300–950 cm^{-1} for different reaction products.

Compound	Wavenumber (cm^{-1})	Compound	Wavenumber (cm^{-1})
PI + 2-butanol		TBTM + PI + 2-butanol	
	1232.6		1233.3
	1176.4		1216.9
	1155.9		1192.7
	1097.2		1177.6
	1082.8		1098.1
	1054.6		1082.2
	1029.6		1070.1
			1053.4
			1030.1
PI + methanol		TBTM + PI + methanol	
	1224.1		1235.1
	1192.7		1216.9
	1176.9		1191.8
	1084.4		1178.7
	1069.8		1235.1
	1030.1		1084.1
			1070.2
TBTM			1054.1
	1216.0		1030.1
	1056.4		

PI – phenyl isocyanate, TBTM – tributyltin methoxide.

trend as what is found in the theoretical calculations (Fig. 10). We believe that in the above experiment when TBTM was used as a catalyst the reaction mechanism went through forming a ternary complex as in Fig. 9. However, we think that O-substituted phenyl carbamate (derivative of stannyl phenylcarbonimidate) in an alcohol solvent will not lead to the formation of N-substituted phenyl carbamate (derivative of (stannyl)carbamate). The O-substituted carbamate (derivative of stannyl carbonimidate) will react with alcohol to liberate the urethane from organotin compound and regenerate the organotin alkoxide as found for other dialkyl tin compounds [24]. This is a lower energy pathway compared to the same of N-substituted carbamate. Therefore, the main contribution to the overall rate of the reaction will depend on how the reaction takes place around first transition of the reaction mechanism proposed. Since the trends in reactivates observed in the two solvents agree with our calculation, it suggests that the reaction takes place though an intermediate O-substituted phenyl carbamate (derivative of stannyl phenylcarbonimidate). This conclusion is based on the enthalpy and free energy calculated for both starting van der Waals complexes as stated previously. Fig. 8 shows that the IRC for the N-coordinated reaction pathway in polar and non-polar media. The IRC data show the activation energy for pathway1 in polar media is higher than in non-polar media. This is contrary to the experimental results shown in Fig. 11.

3.5.1. *FT-IR/ATR investigation on reaction products*

We reacted equimolar amounts of TBTM (tributyltin methoxide) and PI (phenyl isocyanate) with methanol and 2-butanol separately. The alcohol was mixed with TBTM first and subsequently the isocyanate was added to the mixture. As observed in literature the alkoxy urethane absorption in the IR region will be in the range between 1300 and 900 cm^{-1} [35]. However, by comparing the spectra of the reaction products the most significant differences were in the region between 1400 and 1000 cm^{-1}. Since we were not able to find reference absorption to our compounds we compared the absorption in the selected region in a systematic way. Fig. 12 shows the FT-IR/ATR absorption spectra for reaction products of different combination of reagents. These spectra were obtained at 50% concentration in chloroform. Table 3 shows the absorption values for each reaction product in the 1300–900 cm^{-1} region. From Fig. 12(a) it can be seen that the reaction products of PI + 2-butanol and PI + methanol show distinct absorptions at 1235 cm^{-1}, 1055 cm^{-1} (PI + 2-butanol) and 1224, 1070 cm^{-1} (PI + methanol), respectively. It can also be seen in Fig. 12(b) that the reaction products of TBTM + PI + 2-butanol has absorption peaks closely resemble for the absorption of PI + 2-butanol. However, there is also an absorption at 1070 cm^{-1}, which is found in reaction products of PI + methanol. This indicates TBTM + PI + 2-butanol contains reaction products similar to PI + 2-butanol and PI + methanol. The absorption in the range 1053–1057 cm^{-1} is found in PI + 2-butanol as well as in TBTM. This absorption can be seen in the spectrum of TBTM + PI + methanol, but with a lower intensity as in the TBTM + PI + 2-butanol mixture. Overall, the absorption bands observed for the reaction products of TBTM + PI + methanol correspond to the absorptions of the reaction products of PI + methanol with the additional peak at 1054 cm^{-1}, which should be due to TBTM being present in the reaction product. Although the absorption due to TBTM and reaction products of PI + 2-butanol overlap the strong absorption at 1054 cm^{-1} for the TBTM + PI + 2-butanol indicates the formation of PI + 2-butanol reaction products in addition to TBTM present in the reaction product mix. Free energy calculations of the interaction between TMTM and isopropanol to convert to TMT isopropoxide and methanol result in 7.2 and 10.3 kJ mol^{-1} for enthalpy and free energy at 289 K, respectively, at the DFT/B3LYP LANL2DZ/6-31G* level of theory. This indicates

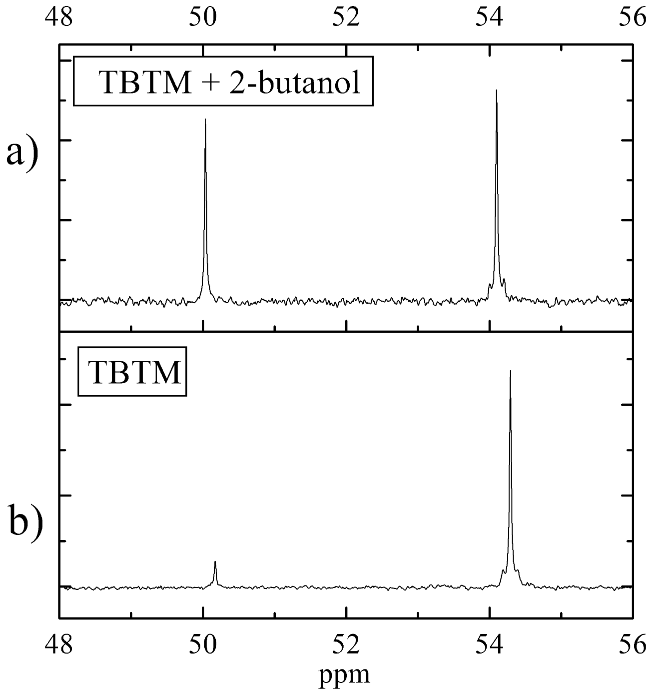


Fig. 13. ^{13}C NMR spectrum for (a) mixture of TBTM and 2-butanol and (b) TBTM (97% in methanol).

that organotin with primary alkoxide is lower in energy than with a secondary alkoxide. If the initial interaction is with organotin alkoxide and phenyl isocyanate through N-coordination then it should give urethane that is formed as a result of phenyl isocyanate reacting with methanol. Since the two products are different the mechanism can be explained as going through a ternary complex, shown in Fig. 9, complex 2. This suggests that even if the interaction between the trialkyltin alkoxide and isocyanate is between Sn and N, in the presence of alcohol the interaction should be realized through a Sn—O mechanism. However, our computational work gives more evidence for the interaction between trimethyltin methoxide and phenyl isocyanate to have an O-coordination rather than a N-coordination due to a more stable van der Waals complex that is formed in the beginning of the interaction, albeit the N-coordination gives a lower energy transition state. Enthalpies and free energies of the formation for the N-coordinated and termolecular O-coordinated van der Waal complexes are 20.9, −27.5 and 56.9, 52.6 kJ mol^{-1} at 298 K, respectively, calculated using DFT/B3LYP LANL2DZ/6-31G* level of theory. From these results the O-coordinated termolecular route is a possibility.

3.5.2. ^{13}C NMR studies on reaction products

To study the complex formation of samples of TBTM with 2-butanol, ^{13}C NMR measurements have been conducted (by using $CDCl_3$ as solvent). Fig. 13(a) shows ^{13}C NMR spectra for methoxy and methanol carbons after mixing TBTM with 2-butanol (at a 1:1 mole ratio). For comparison, Fig. 13(b) shows the ^{13}C NMR spectra for the methoxy and methyl alcohol carbons at 54.24 and 50.12 ppm for TBTM (97% in methanol), respectively. An increase in intensity of the carbon signal relative to methanol can be observed. This indicates a possibility of exchanging some percentage of methoxy with 2-butoxy groups. These data agree with the theoretical results of the alcoholysis of TMTM with iso-propyl alcohol, as discussed in the previous section. Fig. 14 shows the depletion of NCO content with time for the reaction between aromatic p-MDI with 1-butanol and

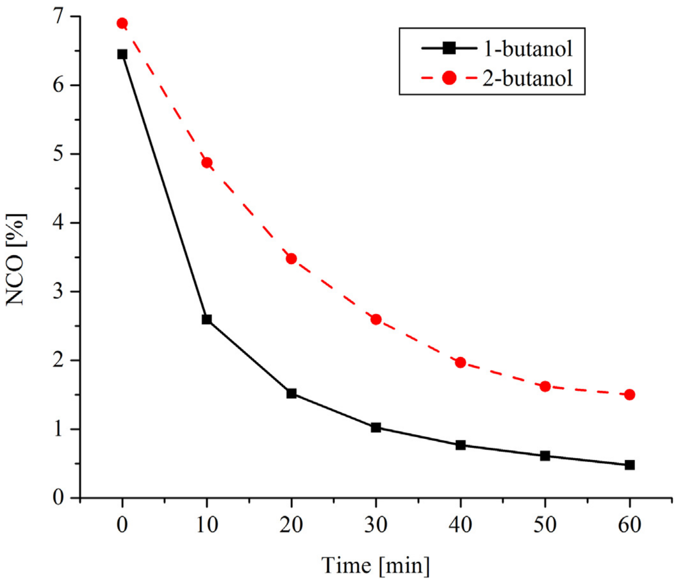


Fig. 14. Depletion of the NCO content in the reaction of p-MDI and (a) 1-butanol (b) 2-butanol in xylene using TBTM as a catalyst (Sn content 0.072 g).

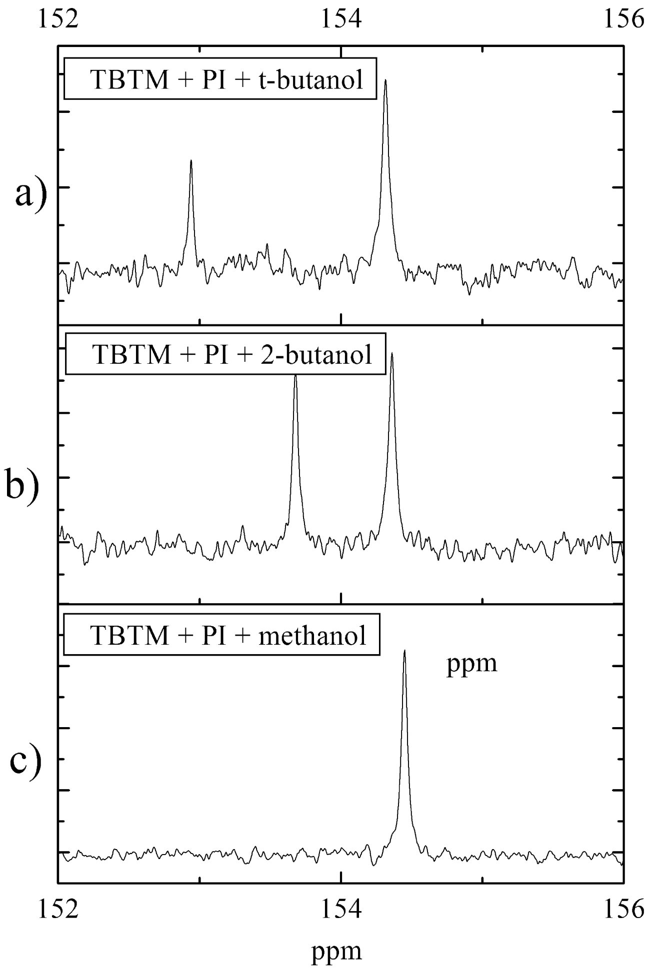


Fig. 15. ^{13}C NMR urethane carbon for reaction products of the (a) TBMT, phenyl isocyanate and tert-butanol (1:1:1 mole ratio), (b) TBTM, phenyl isocyanate and 2-butanol (1:1:1 mole ratio), and (c) TBTM, phenyl isocyanate and methanol (1:1:1 mole ratio).

2-butanol using TBTM as catalyst. In this set of experiments the same amount of TBTM catalyst (0.072 g tin) was used. It is evident that 1-butanol has a higher reactivity towards aromatic isocyanate in the presence of TBTM as the catalyst than 2-butanol. This indicates that the possibility of the formation of urethane by using 2-butanol is less probable if the interaction between the isocyanate and TBTM is through N-coordination or O-coordination without another molecule of alcohol. This mechanism will be discussed in the following paragraph.

Fig. 15 shows the ^{13}C NMR spectra of the urethane carbon for the reaction products of the (a) TBMT, phenyl isocyanate and tert-butanol (1:1:1 mole ratios), (b) TBTM, phenyl isocyanate and 2-butanol (1:1:1 mole ratios) and (c) TBTM, phenyl isocyanate and methanol (1:1:1 mole ratios). Fig. 15(c) shows a peak at 154.38 urethane carbonyl carbon due to methanol. Fig. 15(b) shows two peaks at 154.36 and 153.68 ppm, corresponding to the methoxy and 2-butoxy groups present in urethane. This indicates that both urethanes are present in the sample that contains TBTM, phenyl isocyanate and 2-butanol. Since TBTM contains 3% methanol this would have contributed to the final percentage of urethane correspond to methanol. Similarly, Fig. 15(a) shows two peaks due to formation of urethane between phenyl isocyanate and methanol and phenyl isocyanate and tert-butanol corresponding to the urethane that has alkoxy group methoxy and 2-butoxy at 154.32 and 152.95 ppm, respectively. Therefore in the reaction between TBTM, phenyl isocyanate and 2-butanol if the reaction is realized via N-coordination then the product should contain a higher percentage of urethane that is mainly formed due to reaction with the methoxide. The possible mechanisms of the reactions are shown in Schemes 2–4.

From Fig. 14 it is evident that secondary alkoxy derivatives are less reactive than primary alkoxy derivatives of TBTM. We have assumed that during reaction TBTM as a catalyst is converted to corresponding derivative of the alcohol. However, the NMR results indicate that the reaction is possible to go through an alternate mechanism. The reaction can go through O-coordination with an alcohol molecule to form a more stable van der Waals complex compared to a complex formed through N-coordination. When tert-butanol was used instead of 2-butanol the reaction products indicate a similar outcome with urethane correspond to tert-butanol. Since the energy of the van der Waals complex for the N-coordination is higher than O-coordinated complex, the mechanism through O-coordination without an alcohol molecule is also a possibility. Theoretical calculations show that both O-coordinated mechanisms have similar activation energies (toluene) indicating that the selection will depend on curvature of the IRC plots (see Figs. 8 and 10). The termolecular mechanism also leads to elimination of a molecule of methanol, which could react to give urethane that contain methoxy group. These data strongly support the proposed mechanism.

3.6. *Comparison of catalytic effect of TBTM and DBTDA in aromatic systems*

We also reacted p-MDI and 1-butanol in xylene in the presence of DBTDA (dibutyltin diacetate) as the catalyst and compared it with TBTM (tributyltin methoxide) as the catalyst (tin content 3.768×10^{-3} g). Fig. 16 shows the depletion of the NCO content with time for both runs. From the figure it can be seen that the catalytic effect for DBTDA is much higher compared to TBTM with respect to the tin content in the catalyst quantities used. In our earlier work we have proposed that in case DBTDA is used as catalyst in an aromatic system, the dominant catalyst is the alkoxide, which is formed as an intermediate [24]. Based on this result we carried out theoretical investigations at DFT/B3LYP LANL2DZ/6-31+G** level of theory, using the CPCM solvent model with toluene as solvent, for the N-coordinated and termolecular O-coordinated mechanism for TMTM (trimethylttinmethoxide) and DMTDM (dimethytin dimethoxide) catalyzed reactions between phenyl isocyanate and methyl alcohol. Fig. 17 shows the IRC for both DMTDM and TMTM catalysts for both mechanisms. The activation energies of DMTDM for both mechanisms are close to the N-coordinated mechanism of TMTM. For the termolecular O-coordinated mechanism there is a significant difference in the curvature indicating an additional catalytic effect in the reaction (9.4 kJ mol^{-1} at IRC = 0), whereas for the N-coordinated mechanism the difference is almost negligible (0.6 kJ mol^{-1} at IRC = 0). The termolecular reaction mechanism proposed support the observed results in the presence of different catalysts.

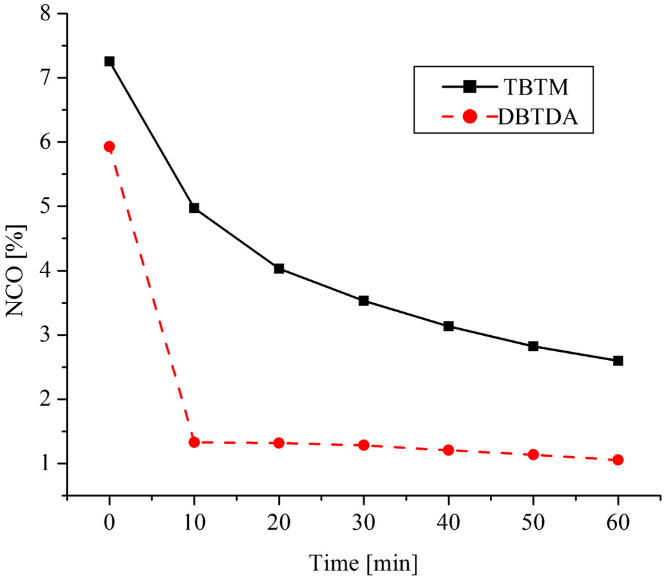


Fig. 16. Depletion of NCO % in the interaction between phenyl isocyanate and 1-butanol at stoichiometric amounts in the presence of amounts of TBTM and DBTDA as catalyst.

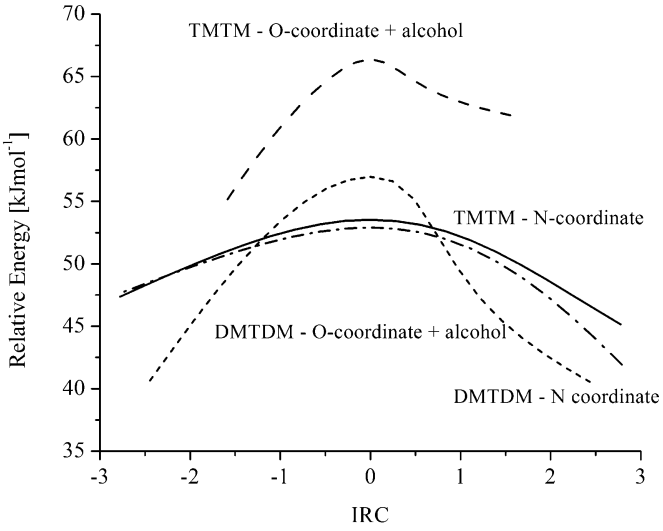
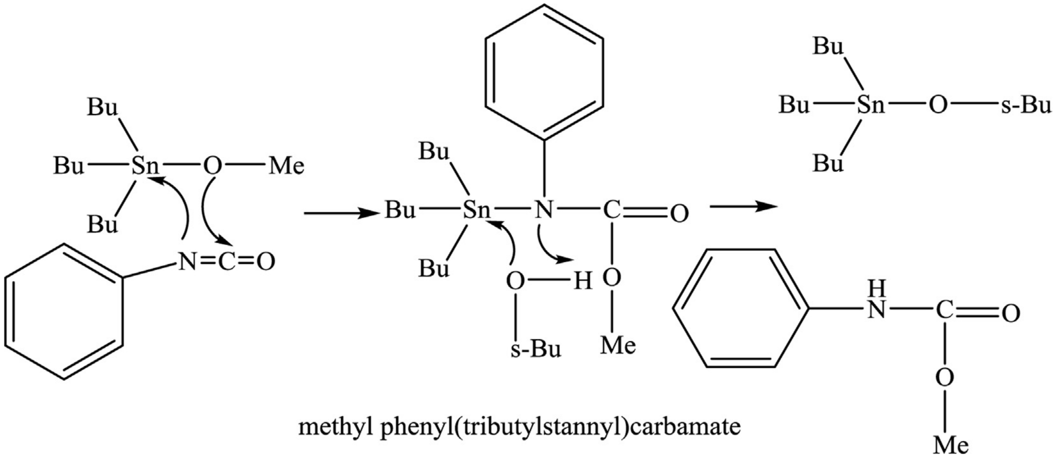
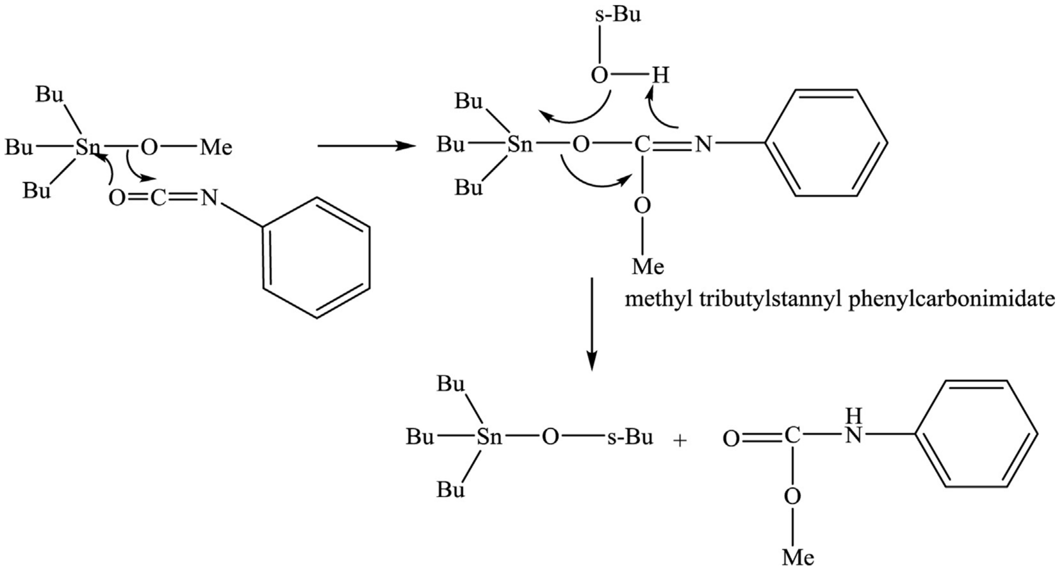


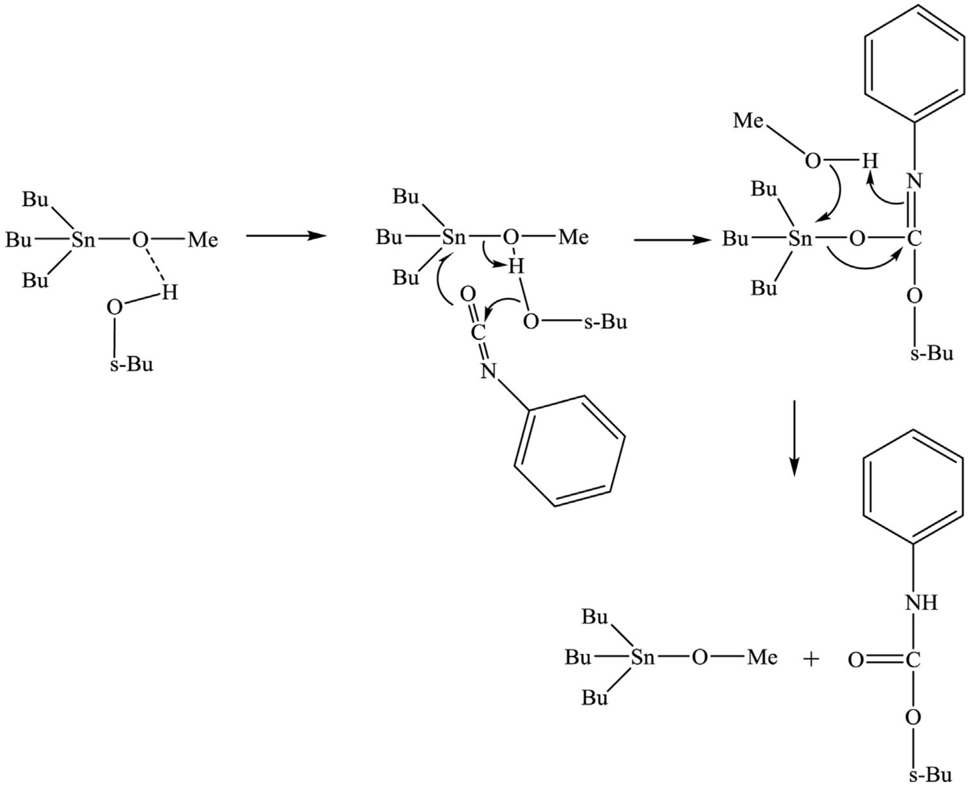
Fig. 17. IRC data for the transition state for TMTM and DMTDM as catalyst for the interaction between phenyl isocyanate and methyl alcohol for termolecular mechanism.



Scheme 2. Reaction mechanism for the interaction between phenyl isocyanate and TBTM in the presence of 2-butanol. Initial coordination through nitrogen of the isocyante and tin of TBTM.



Scheme 3. Reaction mechanism for the interaction between phenyl isocyanate and TBTM in the presence of 2-butanol. Initial coordination through oxygen of the isocyante and tin of TBTM.



Scheme 4. Reaction mechanism for the interaction between phenyl isocyanate and TBTM in the presence of 2-butanol. Formation of a termolecular complex between TBTM, 2-butanol and phenyl isocyanate.

4. Conclusion

The experimental products reported by Bloodworth and Davies for the intreaction between tryalkyl tin methoxide and isocyanate agree with the computational findings. However, computational methods give more information related to the initial interaction between the two reactant molecules. Simulations show that the initial interaction occuers between the oxygen of the isocyanate and the tin center which indicates that the dominant interaction between the organotin compund and isocyanate can be mainly discribed as Lewis interaction. After the initial interactiona and by keeping the same orientation the molecule will undergo an insertion reaction to form the O-substituded carbamate. Once the insertion reaction is compleated the molecule will rearrage to N-substitited carbamate as the final compound as reported by Bloodworh and Davies. When TBTM is acting as a catalyst the reaction will take a termolecular mechanism.

Acknowledgements

The authors thank Uroxsys Ltd., Auckland, New Zealand, for the financial support of this project. The authors are also very grateful for the support provided by Computational Chemistry Group at the School of Chemical Sciences, the Centre for eResearch, The University of Auckland, and NESI New Zealand. The authors also thank Dr. Michael Schmitz (NMR facility at the Faculty of Sciences, The University of Auckland), for his assistance.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.08.003.

References

[1] A.J. Bloodworth, A.G. Davis, J. Chem. Soc. (1965) 5238–5244.
[2] D. Randall, S. Lee, The Polyurethanes Book, John Wiley & Sons, Ltd., 2010.
[3] M. Szycher, Szycher's Handbook of Polyurethanes, CRC Press, New York, 1999, pp. 1–20.
[4] J. Robins, J. Appl. Polym. Sci. 9 (1965) 821–838.
[5] R.P. Houghton, A.W. Malvaney, J. Organomet. Chem. 518 (1996) 21–27.
[6] F.W. van der Weij, J. Polym. Sci., Polym. Chem. Ed. 19 (1981) 381–388.
[7] S.l. Reegen, K.C. Frisch, J. Polym. Sci. 8 (1970) 2883–2898.
[8] H.A. Smith, J. Appl. Polym. Sci. 7 (1963) 85–95.
[9] R. Bacaloglu, L. Cotarcâ, N. Marcu, S. Tölgyi, J. Prakt. Chem. 330 (1988) 541.
[10] K.K. Majumdar, A. Kundu, I. Das, S. Roy, J. Appl. Organomet. Chem. 14 (2000) 79–85.
[11] M. Ratier, D. Khatmi, J.G. Duboudin, Appl. Organomet. Chem. 6 (1992) 293–296.
[12] Tin Chemistry Fundamental, Frontiers and Applications, John Wiley & Sons, 2008, pp. 93–116, 269–283, 681–700.
[13] A.L. Silva, J.C. Bordado, Catal. Rev. 8 (2004) 31–51.
[14] K.C. Frisch, L.P. Rumao, J. Macromol. Sci. Rev. Macromol. Chem. 5 (1970) 103–150.
[15] G. Raspoet, M.T. Nguyen, M. McGarraghy, A.F. Hegarty, J. Org. Chem. 63 (20) (1998) 6878–6885.
[16] A.Y. Samuilov, L.A. Zenitova, Y.D. Samuilov, A.I. Koanovalov, Russ. J. Org. Chem. 44 (2008) 1316–1322.
[17] A.Y. Samuilov, L.A. Zenitova, Y.D. Samuilov, A.I. Koanovalov, Russ. J. Org. Chem. 45 (2009) 68–73.
[18] A.Y. Samuilov, L.A. Zenitova, Y.D. Samuilov, A.I. Koanovalov, Russ. J. Org. Chem. 46 (2010) 1452–1460.
[19] M. Hatanaka, Bull. Chem. Soc. Jpn. 82 (2009) 1149–1151.
[20] M. Coban, F. Aylin, S. Konuklar, Comput. Theor. Chem. 963 (2011) 168–175.
[21] N. Malwitz, J. Phys. Chem. 99 (1995) 5291–5298.
[22] N. Malwitz, CAChe Connect. 1 (1992) 6–8, CAChe scientific, P.O. Box 500, MS 13-400, Beaverton, OR.
[23] M. Hatanaka, Bull. Chem. Soc. Jpn. 84 (2011) 933–935.
[24] R. Devendra, N.R. Edmonds, T. Söhnel, J. Mol. Catal. A: Chem. 366 (2013) 126–139.
[25] H.B. Schlegel, J. Comput. Chem. 3 (1982) 214–218.
[26] H.P. Hratchian, H.B. Schlegel, J. Chem. Phys. 120 (2004) 9918–9924.
[27] H.P. Hratchian, H.B. Schlegel, J. Chem. Theory Comput. 1 (2005) 61–69.
[28] V. Barone, M. Cossi, J. Phys. Chem. A 102 (1998) 1995–2001.
[29] M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 24 (2003) 669–681.
[30] M.J. Frisch, G.W. Trucks, 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.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.

[31] 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. Spartan'10 Wavefunction Inc., Irive, CA; W.J. Hehre, A Guide to Molecular Mechanics and Quantum Chemical Calculations, Wavefunction, Inc., Irvine, CA, 2011.

[32] ASTM-D2572-97, Standard Test Method for Isocyanate Group in Urethane Materials or Prepolymers, ASTM International, West Conshohocken, PA 19428, 2010.

[33] E. Kraka, D. Cremer, Acc. Chem. Res. 43 (2010) 591–601.

[34] Z. Konkoli, E. Kraka, D. Cremer, J. Phys. Chem. A 101 (1997) 1742–1757.

[35] J. Bandekar, S. Klima, J. Mol. Struct. 263 (1991) 45–57.