

Catalytic Mechanisms of Triphenyl Bismuth, Dibutyltin Dilaurate, and Their Combination in Polyurethane-Forming Reaction

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ABSTRACT: The catalytic mechanisms of triphenyl bismuth (TPB), dibutyltin dilaurate (DBTDL) and their combination have been studied in a model polyurethane reaction system consisting of copolyether (tetrahydrofuran–ethyleneoxide) and N-100; NMR spectroscopy was used to detect the associations between reactants and catalysts. A relatively stable complex was shown to be formed between hydroxyl and isocyanate; the catalysts showed different effects on the isocyanate–hydroxyl complex, therefore resulting in different curing characteristics. The formation of hydrogen bonding between the complexed hydroxyl and other hydroxyl or the resulting urethane provided an “auto-catalysis” to urethane formation. DBTDL destroyed the isocyanate–hydroxyl complex before catalyzing the reaction through the formation of a ternary complex, whereas TPB was able to activate the isocyanate–hydroxyl complex directly to form urethane. The reaction catalyzed by the combination of TPB and DBTDL gained advantages from the multiple catalytic entities, i.e., TPB, DBTDL, and a TPB–DBTDL complex. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1217–1225, 1997

Key words: catalytic mechanism; urethane polymer; NMR spectroscopy; triphenyl bismuth; dibutyltin dilaurate

INTRODUCTION

Catalysis in the reaction of urethane formation is often complicated by the fact that urethane formation is subject to multiple side reactions and that the presence as well as the choice of catalyst may have considerable influence on the ultimate properties of the resulting polymer. The most important reactions in the preparation of polyurethanes are the reaction between isocyanate and hydroxyl (chain propagation reaction) and the reaction between isocyanate and water (foaming re-

action). The functions of catalysts employed in urethane formation generally lie in (1) bringing about faster rates of reactions; (2) establishing a proper balance between the chain propagation reaction and the foaming reaction; and (3) bringing about completion of the reactions, hence resulting in an adequate “cure” of the respective polymer.^{1–3} The catalysts most commonly used are tertiary amines and metal catalysts, especially tin catalysts. It is well known that organotin compounds are extremely effective for the isocyanate–hydroxyl reaction, while tertiary amines are catalysts for both the isocyanate–hydroxyl and the isocyanate–water reactions.^{2,4}

Over the past few years, however, a new cata-

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lyst, triphenyl bismuth (TPB), has found increasing use in the preparation of polyurethanes, especially in curing urethane binders for solid propellants.⁵⁻⁹ A combination of TPB with dibutyltin dilaurate (DBTDL) is usually used instead of TPB alone. It has been experimentally found that TPB was relatively low in catalytic activity, while DBTDL resulted in erratic cures, sometimes producing grains with tacky surfaces, and that both catalysts caused unacceptable gassing.⁷ However, when the two catalysts were simultaneously used, DBTDL appeared to provide the major driving force for the curing reaction and activate the TPB for catalytic purposes, whereas TPB tended to moderate the reaction and produce consistent and complete curing process.⁷⁻⁹ The curing rates and pot life can be easily varied and controlled by adjusting the ratio and level of the two catalysts. It seemed that the combination of these two catalysts strongly promoted the isocyanate-hydroxyl reaction compared to the isocyanate-water reaction because void-free propellant with satisfactory process parameters and improved mechanical properties was able to be achieved.⁷

Although polyurethane reactions have been subjected to a great number of studies which have resulted in various mechanisms for the urethane formation,¹⁰⁻¹² very little attention has been paid to the mechanistic aspects of TPB and its combination with DBTDL. Particularly, so far none of the proposed mechanisms could give satisfactory interpretations on the above-mentioned experimental results.

In this work, efforts were made to gain insight into the catalytic mechanisms of TPB and DBTDL. A typical formulation for a propellant binder system consisting of a polymeric isocyanate (N-100) and a polyether polyol (THF/EO copolyether) was selected as a model reaction. NMR spectroscopy was used to investigate the associations and complex formations between reactants and catalysts. The discussion will focus on the mechanistic implications of the obtained results.

EXPERIMENTAL

Materials

Co-polyether of tetrahydrofuran and ethyleneoxide (PTE), segmental ratio of THF/EO = 40/60, was supplied by Liming Institute of Chemical Technology with a number-average mol. wt of

4055, a heterogeneity index of 1.42, an average functionality of 1.81, and an OH value of 25.01 mg KOH g⁻¹ polyol. It was purified by precipitation into excess *n*-hexane, then the precipitate was washed three times with *n*-hexane and finally dried at 90°C for 2.5 h under vacuum. N-100 was supplied by Liming Institute of Chemical Technology, having an average functionality of 4.5, a number-average mol. wt of 982, and a heterogeneity index of 1.50. TPB and three isomers of tris(ethoxyphenyl)bismuthine were synthesized by Shanghai Institute of Organic Chemistry and used as received. Analytical grade DBTDL was dehydrated over 3-Å molecular sieves prior to use. Deutero-chloroform (CDCl₃), NMR reagent, was used as solvent without further purification. Carbon tetrachloride (CCl₄), was analytical grade and was dried overnight with calcium hydride and 3-Å molecular sieves before use as solvent.

The 0.1 mol L⁻¹ solutions of the samples were prepared by dissolving in CDCl₃ or CCl₄ solvents. All glassware, including NMR tubes (5 mm o.d.), were dried overnight at 100°C before use.

NMR Experiments

All NMR measurements were performed on a Varian UNITY-400 spectrometer with ¹³C operating at 100.58 MHz. Five-mm o.d. NMR tubes were used. When CCl₄ was used as solvent, a capillary containing dimethyl sulfoxide (DMSO) was inserted into the NMR tube to maintain a lock signal. Chemical shifts were reported in terms of the parameter δ in ppm and were referenced internally by setting $\delta_{\text{CDCl}_3} = 77.00$ for ¹³C and $\delta_{\text{TMS}} = 0.00$ for ¹H.

¹³C-NMR spectra were recorded at the operating frequency of 100.58 MHz with reverse-gated decoupling mode; a 90° pulse of 14 μ s and repetition time of 7.0 s were employed; sweep width and data points were 20 kHz and 16 K, respectively. An accumulation of > 5000 FID signals were collected. ¹H-NMR spectra were obtained at 399.95 MHz with a 90° pulse of 25 μ s and repetition time of 2.3 s. Spectral width and data points were 4.2 kHz and 64 K, respectively; usually 32 transients were accumulated.

Spin-lattice relaxation time (T_1) was determined for some solutions with the "inversion-recovery" method.

RESULTS AND DISCUSSION

Isocyanate–Hydroxyl Complex and Autocatalysis of Hydroxyl and Urethane

The solution structures of PTE and N-100 have been previously studied by high-resolution NMR spectroscopy.^{13,14} The isocyanate carbons in N-100 solution resonate as a single sharp peak at $\sim \delta$ 121, whatever the concentration. The hydroxyl-linked carbons of PTE produce two peaks which are centered at $\sim \delta$ 61 and assigned to free and hydrogen-bonded hydroxyls, respectively. On mixing the solutions of PTE and N-100, however, two adjacent peaks were observed at $\sim \delta$ 121 and a single broadened peak appeared at δ 61, as shown in Figure 1. It is obvious that the spectral changes resulted from the interaction between isocyanate and hydroxyl.

The measurements of T_1 indicated that the downfield one of the two isocyanate peaks had a T_1 of 6.86 s, very close to that of the original single peak ($T_1 = 5.50$ s) in N-100 solution, while the upfield one had a much smaller T_1 of 2.83 s. This

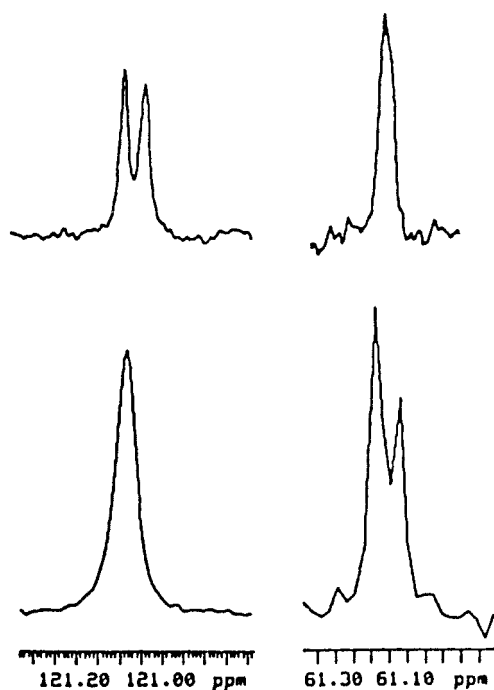


Figure 1 Changes of ^{13}C -NMR spectra of isocyanate carbons and hydroxyl-linked carbons when mixing the CDCl_3 solutions of PTE and N-100. Bottom: spectra of PTE (right) or N-100 (left) solution ($[\text{OH}] = 6.10 \text{ mol L}^{-1}$; $[\text{NCO}] = 6.10 \text{ mol L}^{-1}$). Top: spectra of mixed solution ($[\text{NCO}] = [\text{OH}] = 3.05 \text{ mol L}^{-1}$).

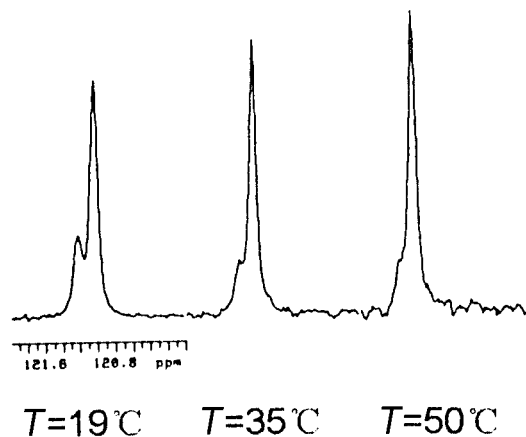
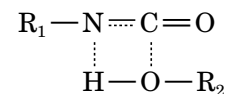
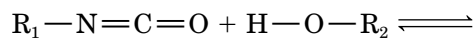


Figure 2 Effect of temperature on the ^{13}C -NMR spectra of associated isocyanates and free isocyanates in CDCl_3 solution ($[\text{NCO}]/[\text{OH}] = 1.2$; $[\text{NCO}] = 5.56 \text{ mol L}^{-1}$).

clearly suggested that the upfield peak represented the isocyanate associated with hydroxyl (referred to hereafter as “associated isocyanate”) and the downfield one was free from the association (referred to as “free isocyanate”).

When the temperature of the mixed solution increased, the associated isocyanate peak became enhanced while the free isocyanate peak was weakened. Meanwhile, the two peaks were approaching and tended to be overlapped (see Fig. 2). This indicated that some free isocyanates were converted into associated isocyanates and that the exchange rate of the two increased, which cannot be explained in terms of hydrogen bonding. In addition, the upfield location of the associated isocyanate peak implied that an increased electron density appeared in carbon as compared with the free isocyanate.

These results gave evidence to the formation of isocyanate–hydroxyl complex in which the hydroxyl hydrogen was hydrogen-bonding to the isocyanate nitrogen, while the nucleophilic hydroxyl oxygen associated with the electrophilic isocyanate carbon, resulting in an increased electron density in the carbon of associated isocyanate.



This kind of complex was previously postulated in a low-molecular system by Bacaloglu and Co-

tarca¹⁵ and Chang and Chen¹⁶ who, however, failed to supply more direct and convincing evidence. No obvious spectral change was observed when hexamethylene diisocyanate (HDI) was substituted for N-100. This may be explained either by the unstable nature of the complex or by the fast exchange between associated isocyanate and free isocyanate, due to the general fact that low-molecules usually have higher reactivity and mobility than macromolecules. In a macromolecular system, however, this complex is relatively stable.

In the spontaneous reactions of isocyanate with hydroxyl, this complex may serve as an intermediate which is converted into urethane in the subsequent rate-determining step.

The hydroxyl in the complex can be activated by another free hydroxyl (as well as by the resulting urethane) through the formation of hydrogen bonding in which the free hydroxyl (or urethane group) acts as a base catalyst and increases the nucleophilicity of oxygen of complexed hydroxyl.¹⁷

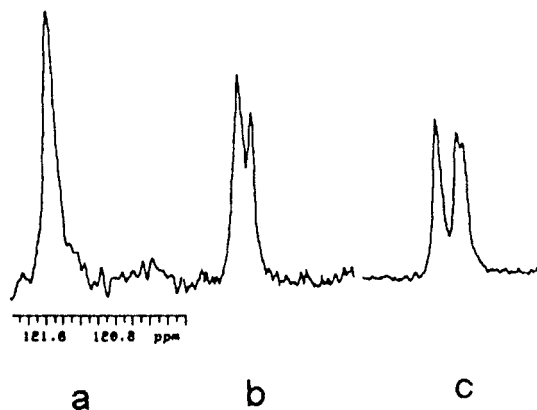
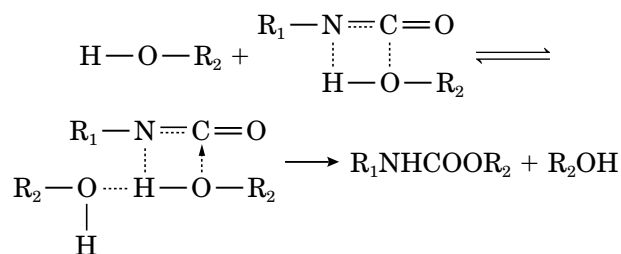


Figure 3 Dependence of the formation of isocyanate-hydroxyl complex on the concentration of PTE/N-100 mixture solution ($[\text{NCO}]/[\text{OH}] = 5.3$; $T = 19^\circ\text{C}$; solvent = CDCl_3). (a) $[\text{NCO}] = 1.14 \text{ mol L}^{-1}$; (b) $[\text{NCO}] = 2.22 \text{ mol L}^{-1}$; (c) $[\text{NCO}] = 2.86 \text{ mol L}^{-1}$.

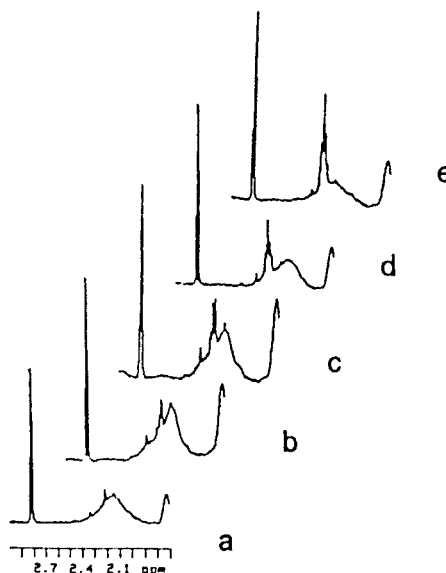


Figure 4 Effect of DBTDL concentration on the ^1H -NMR spectra of hydroxyl of PTE ($[\text{OH}] = 0.04 \text{ mol L}^{-1}$; solvent = CCl_4). (a) no DBTDL; (b) $[\text{Sn}] = 0.001 \text{ mol L}^{-1}$; (c) $[\text{Sn}] = 0.002 \text{ mol L}^{-1}$; (d) $[\text{Sn}] = 0.003 \text{ mol L}^{-1}$; (e) $[\text{Sn}] = 0.006 \text{ mol L}^{-1}$.

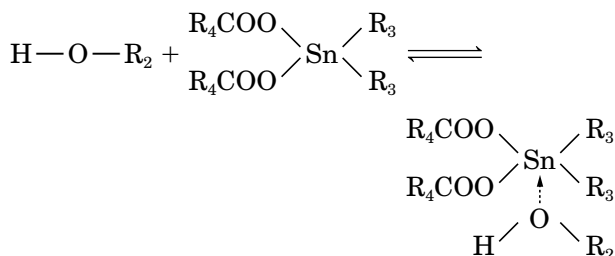
It has also been found that the isocyanate-hydroxyl complex increased with increasing the concentration of PTE/N-100 mixture solution, as can be seen from Figure 3. Consequently, the "autocatalytic" effect¹⁸ observed at high concentration or later stage of curing process can be explained by the autocatalysis of hydroxyl and urethane as well as by the favorable formation of the isocyanate-hydroxyl complex.

Complex Formation Among DBTDL, Hydroxyl, and Isocyanate

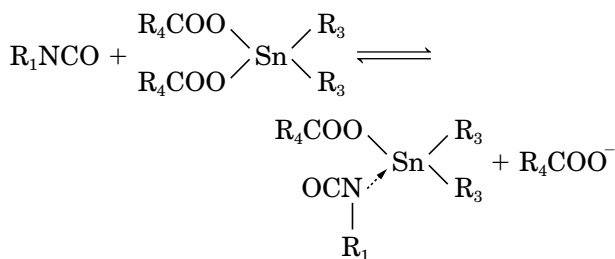
When DBTDL was added to the PTE solution in CCl_4 solvent, it can be seen from Figure 4 that the hydroxyl proton resonance peak was being weakened and tended to disappear with increasing the concentration of DBTDL. This result is in good agreement with those previously obtained in CDCl_3 solvent and in the polyethylene glycol (PEG) system^{19,20} and may be interpreted on the basis of complex formation between DBTDL and hydroxyl, resulting in high mobility of hydroxyl proton which then exchanges with other active protons.²¹



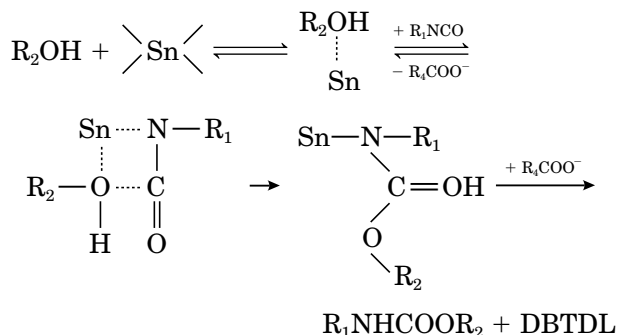
Figure 5 Effect of N-100 on the ^{13}C -NMR spectra of carboxylic carbons of DBTDL in CDCl_3 solution. Bottom: original spectrum of DBTDL. Top: spectrum obtained after addition of N-100.



The formation of the DBTDL–isocyanate complex, which has been shown by other investigators based on IR spectra,^{22,23} was verified by the NMR observation shown in Figure 5 that the resonance peak of carboxylic carbons of DBTDL split into two peaks when N-100 was added into the DBTDL solution. One of the two peaks was assigned to the dissociated carboxylic groups while the other to the associated ones, considering the fact that one of the carboxylic oxygens of DBTDL may be easily replaced by another ligand.¹ The DBTDL–isocyanate complex was assumed to have the following structure.^{3,24}



It appears from the above discussion that DBTDL may complex with both isocyanate and hydroxyl, thus the DBTDL-catalyzed reactions of isocyanate with hydroxyl may be assumed to proceed via the formation of a ternary complex according to the following mechanism, which was similar to that proposed previously by Wongkamolsesh and Kresta.²⁴



It is well known that DBTDL is extremely effective for the propagation reactions (isocyanate–hydroxyl reactions),² which can also be inferred from the above mechanism on the basis that DBTDL preferred to activate hydroxyl rather than water due to the higher nucleophilicity of hydroxyl oxygen. On the other hand, the gassing has been found to be attributable to a side reaction between isocyanate and water, leading to the evo-

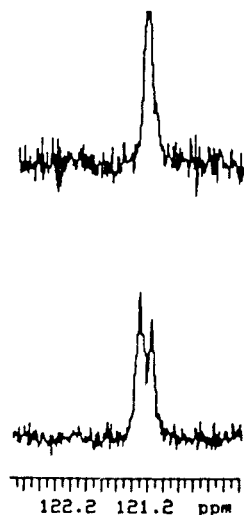


Figure 6 Effect of DBTDL on the isocyanate–hydroxyl complex. Bottom: original ^{13}C -NMR spectrum of PTE/N-100 mixture in CDCl_3 solution. Top: spectrum obtained after addition of DBTDL.

Table I Effect of TPB Concentration on the Chemical Shift and Integral Area of OH Proton Resonance in the CCl₄ Solution of PTE

Sample No.	[OH] (mol L ⁻¹)	[Bi] (mol L ⁻¹)	Chemical Shift (ppm)	Integral Area
1	0.02	0	2.13	0.37
2	0.02	0.01	2.05	0.45
3	0.02	0.02	2.03	0.73
4	0.02	0.04	2.01	1.31
5	0.02	0.06	1.99	1.78
6	0.02	0.08	1.89	2.10

lution of carbon dioxide.⁷ Accordingly, the void formation in the DBTDL-catalyzed system could not be attributed to the mechanism, but resulted from the fast increase in viscosity of the system which made the degassing process difficult.

The above mechanism would require that DBTDL had to destroy the isocyanate-hydroxyl complex before the associated isocyanates and hydroxyls entered into the urethane formation reaction. In deed, DBTDL was capable of doing so, as can be seen from Figure 6, where the associated isocyanates diminished on the addition of DBTDL into the PTE/N-100 mixture solution. Nevertheless, it could be expected that a large amount of isocyanate-hydroxyl complex, a case like in the later stage of the curing process, may be unfavorable for the DBTDL catalysis and responsible for the erratic cures.

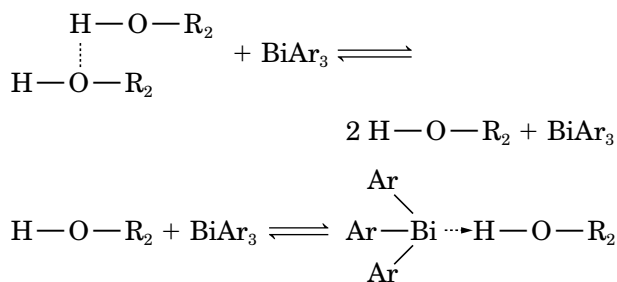
Association of TPB with Hydroxyl and the Catalysis Mechanism of TPB

A study on the interactions in the TPB/PTE system in CCl₄ solution was carried out. As observed from the data in Table I, the hydroxyl proton resonance peak was being enhanced and shifting to upfield with increasing the content of TPB in the mixture solution.

Further efforts have been made to obtain confirmation of the association between TPB and hydroxyl using three isomers of tris(ethoxyphenyl)-bismuthine. Table II illustrated the influence of

the three isomers on the chemical shift of the hydroxyl proton resonance peak. The results indicated that the values of upfield-shifting of the hydroxyl proton decreased in the sequence ortho > para > meta-isomer, in line with the basicity increasing order of bismuth.¹⁹

These results should be attributed to the hydrogen-bonding type association between bismuth and hydroxyl hydrogen, which broke up some hydrogen-bonded hydroxyls and lowered the exchange rate of associated protons with other active protons.^{19,20}



No evidence was obtained for the formation of the TPB-isocyanate associate or complex. The association of TPB with hydroxyl hydrogen increases the nucleophilicity of the adjacent oxygen in the hydroxyl; therefore, the TPB-catalyzed reactions of hydroxyl with isocyanate may be suggested to involve the initial formation of a TPB-hydroxyl associate and a subsequent reaction of the formed

Table II Effect of the Three Isomers of Tris(ethoxyphenyl)bismuthine on the Chemical Shift of OH Proton of PTE in CCl₄ Solution

Sample Composition	PTE in Control	PTE + ortho-isomer	PTE + meta-isomer	PTE + para-isomer
Chemical shift (ppm)	2.749	2.409	2.625	2.518

[OH] = 0.1 mol L⁻¹; [Bi] = 0.05 mol L⁻¹.

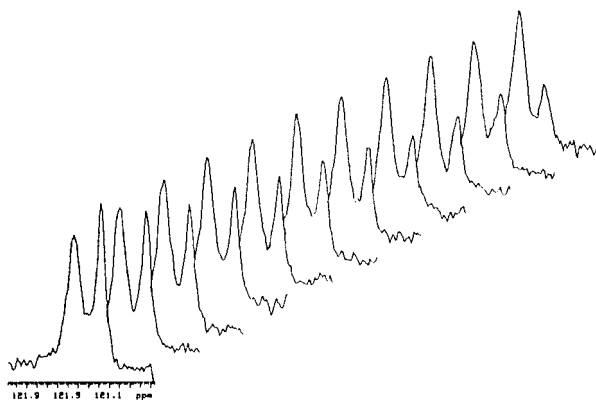
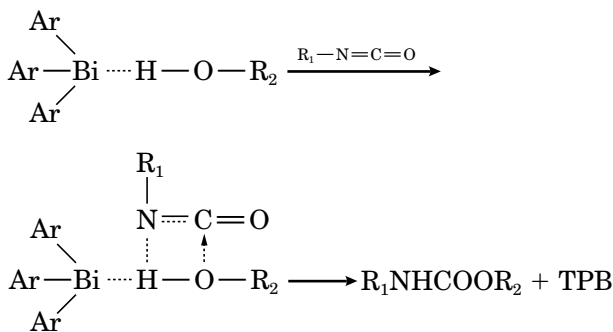


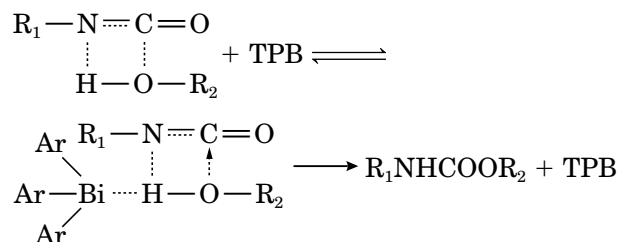
Figure 7 The reaction rates of associated isocyanates and free isocyanates indicated by ^{13}C -NMR spectra in the TPB catalyzed reaction of PTE and N-00. The upfield peak was assigned to associated isocyanates while the downfield peak to free isocyanates. The spectra were acquired at intervals of 1 h in CDCl_3 solution at 35°C and the concentrations of the reaction system were $[\text{NCO}] = 3.06 \text{ mol L}^{-1}$ and $[\text{OH}] = 2.55 \text{ mol L}^{-1}$.

associate with isocyanate, in which the urethane is formed and the TPB catalyst is regenerated.



An alternative pathway for TPB-catalyzed reactions is through the direct activation of TPB on

the existing isocyanate–hydroxyl complex. This mechanism finds a very important support from the kinetic study which indicated that the associated isocyanates reacted much more rapidly than the free isocyanates (see Fig. 7), and may be more operative in high-concentration systems or in the later stage of the curing process, due to the fact that the hydroxyl–isocyanate complex increases with increasing the concentration of PTE/N-100 mixture solution (see Fig. 3). It is apparent that the reason for actually complete and relatively little gassing cures in TPB-catalyzed reactions may be the priority of TPB catalysis through activating the isocyanate–hydroxyl complex, which increases as the reactions proceed.



Mechanism of Combined Catalysis of DBTDL and TPB

Table III summarizes the chemical shifts and integral values of the hydroxyl proton resonance peak when DBTDL and TPB were simultaneously added into the PTE solution. The results indicated that the hydroxyl proton resonance peak was being weakened and shifting downfield with increasing the level of TPB while keeping the level of DBTDL constant, contrary to the results obtained with TPB alone. When keeping the TPB level constant and increasing the DBTDL content, a similar phenomenon was observed.

Table III Effect of the Combined Use of DBTDL and TPB on the Chemical Shift and Integral Area of OH Proton of PTE in CCl_4 Solution

Sample No.	$[\text{OH}]$ (mol L^{-1})	$[\text{Sn}]$ (mol L^{-1})	$[\text{Bi}]$ (mol L^{-1})	Chemical Shift (ppm)	Integral Area
1	0.02	0	0	1.89	2.13
2	0.02	0.001	0.001	1.92	1.59
3	0.02	0.001	0.01	1.96	1.42
4	0.02	0.001	0.02	1.98	1.30
5	0.02	0.002	0.02	2.03	1.14
6	0.02	0.01	0.02	2.12	0.71
7	0.02	0.02	0.02	2.17	0.54

Table IV Effect of DBTDL on the Spin-Lattice Relaxation Time (T_1) of the Carbons and Hydrogens of TPB Measured in 5% (w/v) CDCl_3 Solution at 20°C

Sample Composition	T_1 of C_1	T_1 of $\text{C}_{2,6}$	T_1 of $\text{C}_{3,5}$	T_1 of C_4	T_1 of $\text{H}_{2,6}$	T_1 of $\text{H}_{3,5}$	T_1 of H_4
TPB	11.30 s	3.74 s	3.73 s	2.05 s	4.1 ~ 4.5 s	3.6 ~ 3.9 s	4.2 ~ 4.9 s
TPB + DBTDL (1 : 1)	9.77 s	3.20 s	3.14 s	1.59 s	2.6 ~ 2.7 s	2.2 ~ 2.4 s	2.6 ~ 2.8 s

The subscripts of C and H indicate the position to bismuth.

These spectral changes are similar to those observed with DBTDL alone, suggesting that the combination of DBTDL and TPB showed some nature of DBTDL. It can also be seen from Table III that the weakening rate of the hydroxyl proton resonance peak was a little lower than that of DBTDL alone, correlating with the curing characteristics of the DBTDL/TPB combination that a moderate curing process is usually achieved.

In order to explain these results, an experiment was conducted to check if DBTDL and TPB can form an associate or complex. The results indicated that the spin-lattice relaxation times (T_1) of both carbons and hydrogens in TPB were reduced when DBTDL was added into the TPB solution (see Table IV).

On the basis of these observations and considering the practical catalytic behaviors mentioned in the introduction section, it may be suggested that a complex, similar to the DBTDL–triphenyl phosphine complex,²⁵ might be formed between DBTDL and TPB. The DBTDL–TPB complex might be a catalytic entity with moderate activity that is higher than TPB but lower than DBTDL, and would catalyze the reactions of isocyanate with hydroxyl in a similar mechanism to DBTDL.^{4,25,26}

Due to the existence of multiple catalytic entities, i.e., DBTDL, TPB, and DBTDL–TPB complex, the reactions catalyzed by the combination of DBTDL and TPB take advantage of the high activity from DBTDL, the moderate curing rate from the DBTDL–TPB complex, and the complete cures from TPB. Hence, void-free propellants with satisfactory process parameters and improved mechanical properties could be obtained.

CONCLUSIONS

1. The “auto-catalytic” effect observed in the spontaneous reaction of urethane formation may result from the favorable forma-

tion of a isocyanate–hydroxyl complex as well as from the autocatalysis of hydroxyl and urethane groups.

2. DBTDL was found to be able to complex with both isocyanate and hydroxyl and catalyze the urethane reactions via the formation of a ternary complex. The erratic cures of DBTDL may be attributed to the presence of the isocyanate–hydroxyl complex, which is unfavorable for the DBTDL catalysis, especially in the later stage of the curing process.
3. TPB was shown to be able to associate with hydroxyl. The most operative mechanism of TPB is through activation on the isocyanate–hydroxyl complex, which increases as reactions proceed. Thus, a complete cure with relatively little gassing can be obtained.
4. A complex may be formed between DBTDL and TPB. The advantages of the combined use of DBTDL and TPB result from the multiple catalytic entities, i.e., DBTDL, TPB, and the DBTDL–TPB complex.

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