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Catalysis of the Isocyanate-Hydroxyl Reaction by Non-Tin Catalysts

by

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Abstract

Tin compounds, especially dibutyltin dilaurate, are in widespread use in coatings as catalysts for the isocyanate/hydroxyl reaction. Because of the high aquatic toxicity of some organotin compounds, there has been an attempt to ban organotin compounds from all coating applications. As a general rule organotin catalysts are not selective, they catalyze the reaction of isocyanates with both hydroxyl groups and water and also catalyze the hydrolysis of ester groups. We are interested in finding alternatives to these catalysts and in developing compounds which exhibit increased selectivity for the isocyanate/hydroxyl reaction. In addition, we are interested in developing materials which give a longer potlife and enhanced reaction rates. We will report on various metal salts and chelates we have investigated, the mechanism of catalysis and application characteristics in both high solids and water-borne applications. We found zirconium chelates activates the hydroxyl groups and catalyze the isocyanate-hydroxyl reaction by an insertion mechanism. This reaction is selective and preferred over the isocyanate-water reaction. This permits the use of this catalyst in waterborne isocyanate crosslinked two component coatings. In addition this catalyst permits very high reaction rate which suggests is use in plural component gun applications.

Introduction

The catalysis of the isocyanate-hydroxyl reaction has been studied by many authors¹ who found that the reaction of aliphatic isocyanates with hydroxyl groups is catalyzed by many metal carboxylates and organo tin compounds. t-Amine catalysis of the reaction of aromatic isocyanates with hydroxyl groups has been practiced for some time and is common for the preparation of flexible polyurethane foams². This paper also describes the formation of isocyanurate trimer and the side reaction with water. This side reaction with water is a desirable reaction for foam applications because the thus formed carbon dioxide can be used as a blowing agent. In most coating applications side reaction with water is not desirable because it can lead to gassing and blister formation and also to poor crosslinking density. The water reaction of isocyanates is especially troublesome during cure under high humidity conditions or in two component water-borne isocyanate crosslinked coatings. The reaction of 4,4-dicyclohexylmethane diisocyanate in the presence of dialkyltin compounds with water and alcohols was investigated³ in triethylene glycol dimethyl ether and n-methyl pyrrolidinone. This study found selectivity⁴ of the hydroxyl versus water reaction of between 1.8 to 3.8 depending on reaction conditions. One exception was dibutyltin dichloride which gave equal rate constants for both n-butanol and water. The steric hindrance around the catalytic center was found to have strong effects on the rate constants for urethane reactions catalyzed by sulfonium catalysts⁵. In the cyclotrimerization reaction, this effect on the reaction rate was negligible. The reaction⁶ of isophorone diisocyanate with alcohols was studied in the absence and presence of dibutyltin dilaurate (DBTDL) and 1,4-diazabicyclo[2,2,2]-octane (DABCO). In the presence of DBTDL the reaction of the secondary isocyanate groups was favored, while in the presence of DABCO the reaction of the primary isocyanate group was preferred. Apparently the relative reactivity of the isocyanate group depends on the mode of catalysis and steric hindrance. The reaction of water with aromatic polyisocyanates is of interest in the formation of polyurethane foams. This reaction⁷ was studied in diglyme with amine and tin catalysts. Dibutyltin dilaurate and DABCO gave equal reaction rates with water and hydroxyl groups. Phenylmercuric acetate showed exceptional high reaction rates with water. Surprisingly only 70% of the water was found to contribute to carbon dioxide evolution. In water-borne two component coatings⁸ the formation of urea is a major side reaction. The reaction of polyisocyanates in water-borne two component coatings⁹ in the presence of different amines was investigated. It was observed that the pK_a value of the amine has a large effect on the water-isocyanate reaction and that amines with a higher pK_a value show increased reactivity of the isocyanate with water.

Dibutyltin compounds are generally recognized to function as Lewis acid catalysts by complexing with the isocyanate¹⁰. The mechanism of catalysis of amines has been related to Lewis base catalysis, the amine complexing the alcohol. Indeed a synergistic effect¹¹ of tin compounds with amines has been observed in urethane formation. The observation that the urethane groups formed catalyze¹² the hydroxy/isocyanate reaction complicates in establishing a catalysis mechanism.

We were interested to develop a catalyst which predominately catalyzes the isocyanate-hydroxyl reaction and not the water-reaction. A suppression of the water reaction could permit the formulation of water-borne isocyanate crosslinked coatings with an improved potlife, a reduction in the isocyanate index and also permit a reduction in variation in crosslink density with aging of the formulation.

EXPERIMENTAL

Zirconium dionate complexes used in this study were prepared via ligand exchange reactions¹³ of zirconium compounds with corresponding diketone chelating agents. The different dionate chelating agents were either obtained from commercial sources or were synthesized via the Claisen reaction.

Zirconium catalyst A (ZIRC A) is obtained by preparing a solution of a zirconium, tetrakis(2,4-pentanedionato-kO,kO)-, (SA-8-11"11"1'1"1'1'") complex (ZrAcAc) in 2,4-pentanedione with a metal content of 0.07 %. Zirconium catalyst B (ZIRC B) is a proprietary zirconium tetra-dionato complex¹⁴ in a reactive diluent with a metal content of 0.4 %. The other chelating agents used in the study are identified in the Results Section.

The aluminum chelate catalyst used in this study is an aluminum, tris(2,4-pentanedionato-kO,kO)-, (OC-6-11) complex¹⁵ identified as Alch1.

The bismuth carboxylate catalyst (Bi oct.) used was a commercially supplied 75 % solution of bismuth tris(2-ethylhexanoate)¹⁶ in 2-ethylhexanoic acid.

The polyols and polyisocyanates used during the study were commercial materials and were used without further purification. We observed variations in the reaction rates of the “uncatalyzed reaction” of polyols with polyisocyanates as measured in gel time¹⁷. These variations in reaction rate were attributed to catalytic impurities in both the polyol and also the polyisocyanate and the interaction of impurities with the catalyst. Most of the catalyzed reactions were conducted under conditions to minimize the effect of uncatalyzed catalysis. We also used in our study polyols or polyisocyanates from the same batch or we re-tested new batches for uncatalyzed rates. The gel test was performed by mixing the acrylic polyol¹⁸ with the catalyst, adding the polyisocyanate (HDI-trimer) crosslinker and sealing the blend in a vial. The vials were immersed in a water bath at 62°C and checked for flow and gelation every 5-10 minutes.

Cure studies were conducted on draw down films using a wire applicator. Cure conditions if not indicated were kept at 20-22°C and 50-60 % of relative humidity (RH). Higher temperature cure studies were conducted in a forced air circulating electrically heated oven. The substrate was iron phosphated pretreated steel panels.

Viscosity stability studies were conducted at room temperature (22-25°C) or at a higher temperature as shown in the Result Section in a small sample container. Viscosity was measured on a thermostated Brookfield viscometer equipped with a small sample cup at 25°C and the viscosity was continuously recorded.

For drying time measurement, the liquid formulation containing polyisocyanate, polyol and catalyst was cast on a metal panel and the surface dry time and the through dry time were recorded with a circular Drying Time Recorder¹⁹.

RESULTS

In our initial screening study we used a commercially available acrylic resin and hexamethylene diisocyanate isocyanurate trimer²⁰ (HDI-Trimer) as a crosslinker. As seen in Figure 1 many compounds can catalyze the isocyanate reaction. The gel times in minutes are shown using a metal concentration of 0.01 % metal on the binder resin solids. Dionate indicates a metal dionate complex with 2,4-pentanedione. Me acetac indicates a metal acetoacetate complex. Me oct. are isoctate or 2-ethylhexoate salts of the metal. Napt indicates the naphthenate salt. DBTDL is dibutyltin dilaurate and DBTDA is dibutyltin diacetate. We also screened antimony (III) acetate, zirconium octoate, calcium octoate, titanium tetrabutoxide, chromium (III) dionate and octoate and cerium which showed no catalytic activity. Under different reaction conditions we found titanium tetrabutoxide catalytically active but because of the extreme sensitivity to water the test results are very unpredictable. Both DBTDL and DBTDA showed excellent catalytic activity, closely followed by

the Zr tetrakis(2,4-pentanedionato) complex. It is interesting to note that some of the metal compounds are more catalytic as the carboxylate salts where others are more reactive as the pentanedionate complex.

Because of the high catalytic activity of the zirconium tetrakis(2,4-pentanedionato) complex we decided to further investigate its catalytic activity.

Potlife and tack-free time of polyester/HDI-trimer uncatalyzed and with DBTDL, ZrAcAc catalyzed formulations²¹ was determined. (Figure 2). Although the formulation containing the ZrAcAc catalyst has a substantially shorter potlife that the DBTDL catalyzed system, the tack-free time was significantly larger, raising the question about potential deactivation of the catalyst in the presence of moisture.

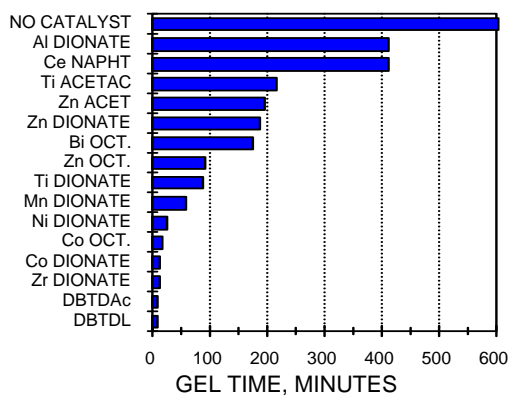


Figure 1 Acrylic Polyol/HDI-trimer 1/1 OH/NCO Nonvolatile 50 % in xylene/butyl acetate, Metal 0.009 % on binder. Temperature 62°C

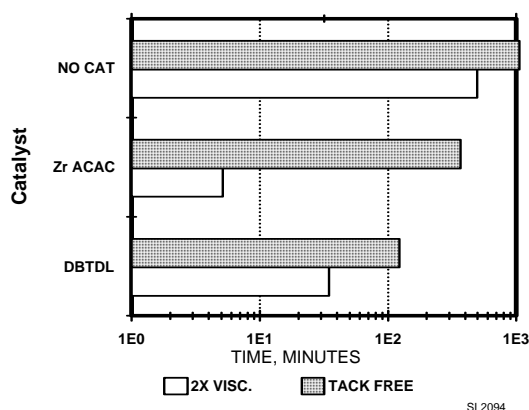


Figure 2 Double viscosity and tack-free time, polyester/HDI-trimer, Catalyst 0.0065 % metal based on resin solids. Temperature 25°C

To increase the potlife and to counteract any potential hydrolysis of the ZrAcAc complex we added 2,4-pentanedione to the formulation equivalent to a 372, 744 and 1343 molar excess respectively. The results are shown in Figure 3. The surprising finding is an increase in the potlife of the formulation and also an improvement in cure response.

To gain further insights in the reaction mechanism of catalysis we synthesized a range of zirconium dionate complexes with a variety of ligands. For the polyol/polyisocyanate component we selected the acrylic resins used in the initial catalyst evaluation. Figure 4 shows the resulting gel, tack-free and dry-through time of a number of zirconium chelates and also comparative information on DBTDL and an the uncatalyzed formulation. Formulations which did not react after 600 minutes did not cure after 720 minutes and required between 12 to 24 hours for cure.

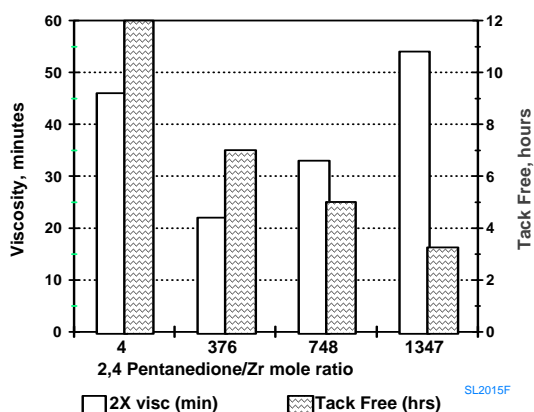


Figure 3. Polyester/HDI-trimer, time for double viscosity in minutes and tack-free time in hours.

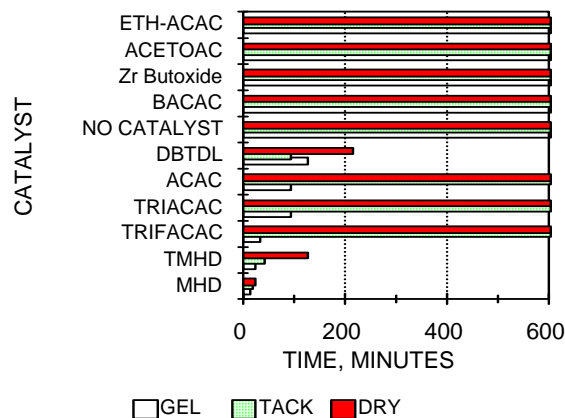


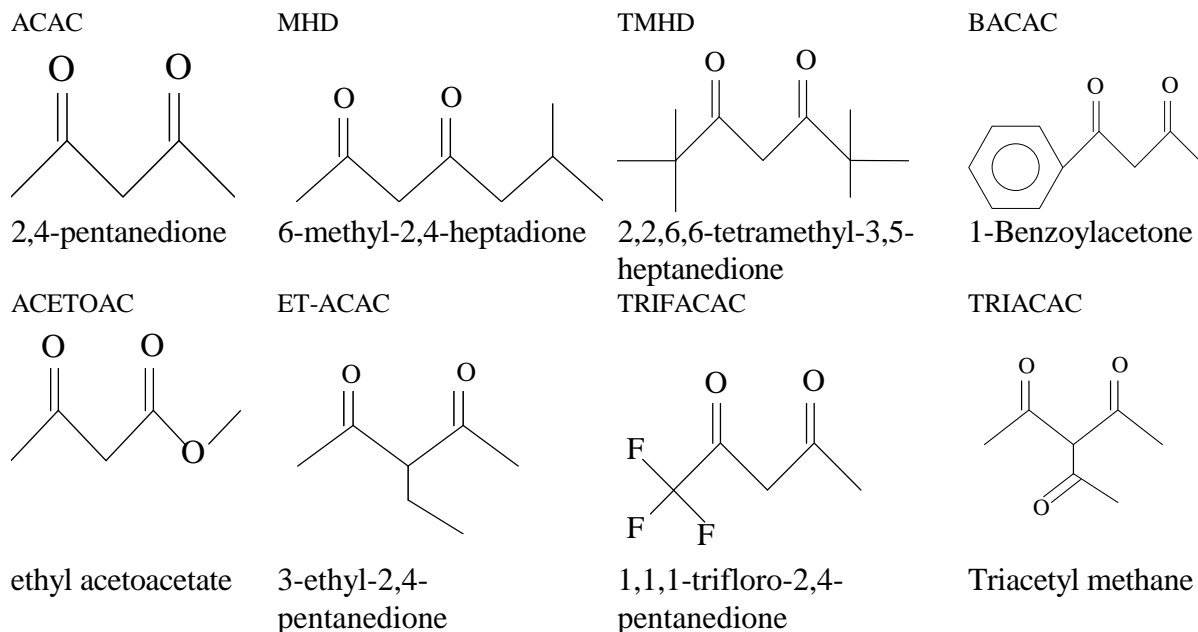
Figure 4. Acrylic/HDI-trimer, gel, tack-free and dry-through time at room temperature. Me 0.0046 %.

Temperature 25°C.

Temperature 25°C

The structure of the chelating agents used is shown in Figure 5. The zirconium complexes were obtained from these ligands by reacting the zirconium alkoxide with 4 moles of the chelating agent and removing the alcohol formed by vacuum distillation. For some of the complexes a diluent or solvent was used for the reaction.

Figure 5. Structure of Ligands



The gel time of acrylic/HDI trimer formulations catalyzed with ZIRC A & B and DBTDL are reported in Figure 6.

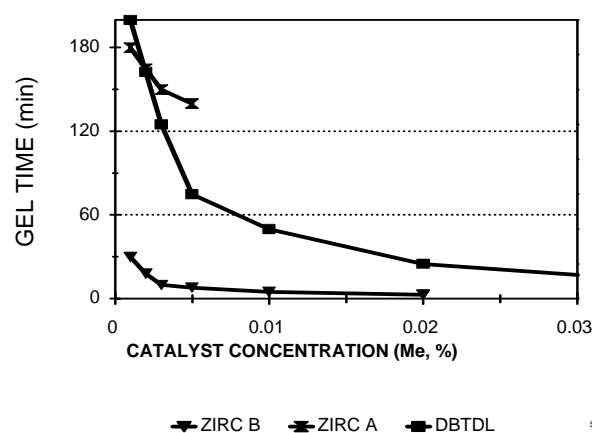


Figure 6 Gel time of acrylic/HDI trimer, gel time for ZIRC A&B and DBTDL. Temperature 25°C.

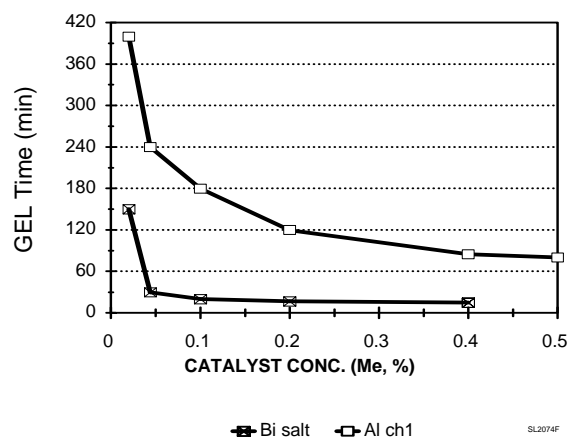


Figure 7. Gel time of acrylic/HDI trimer, gel time for bismuth and Alch1 catalyst. Temperature 25°C.

For the bismuth carboxylate and the Alch1 compounds in Figure 7, the increased gel time of the ZIRC A catalyst is due to the excess 2,4-pentanedione in this material.

Tack-free time for ZIRC A & B and DBTDL is given in Figure 8 and for the bismuth and AlCh1 catalyst in Figure 9.

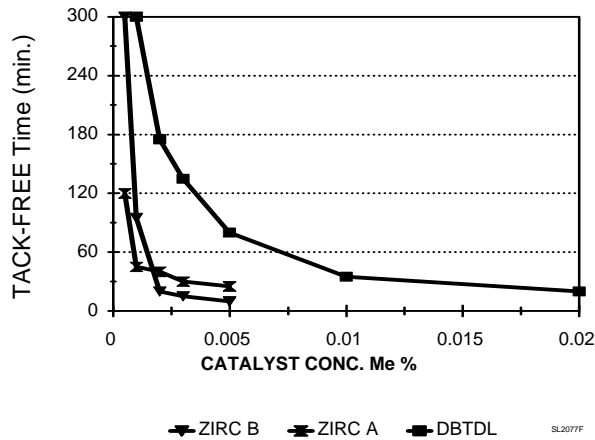


Figure 8. Tack-free time of acrylic/HDI trimer, gel time for ZIRC A & B and DBTDL

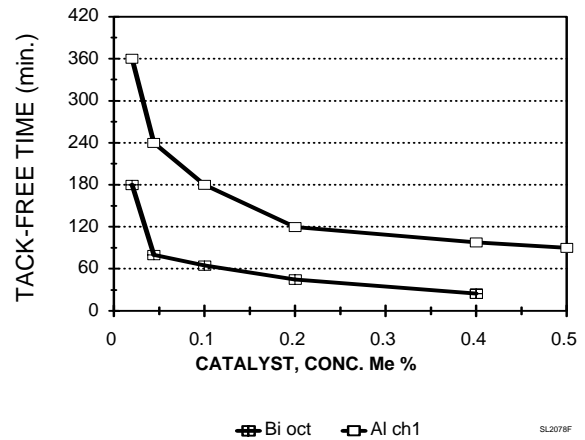


Figure 9. Tack-free time of acrylic/HDI trimer, gel time for bismuth and Alch1 catalyst

Figure 10 and 11 give the dry time for ZIRC A & B, DBTDL and for bismuth and AlCh1 catalyst.

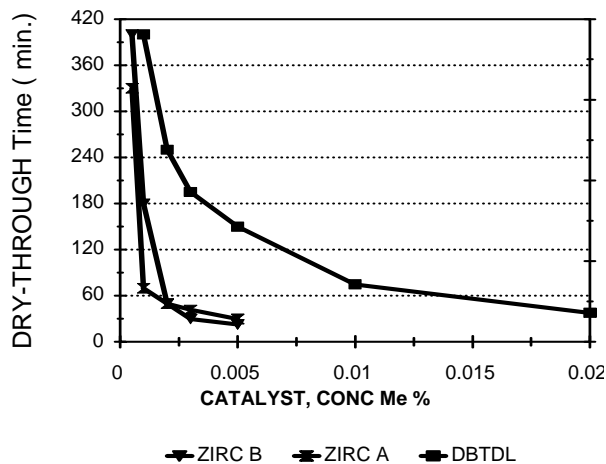


Figure 10. Dry-through time of acrylic/HDI trimer, gel time for ZIRC A&B and DBTDL

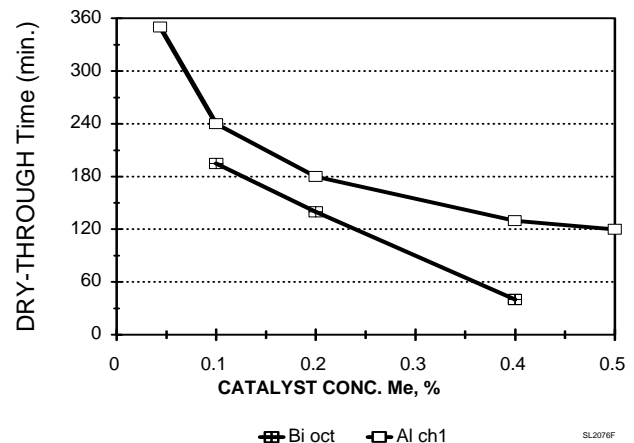


Figure 11. Dry-through time of acrylic/HDI trimer, gel time for bismuth and Alch1 catalyst

The time required for a doubling in viscosity for a polyester/HDI-trimer in the presence of DBTDL and AlCh1 catalyst in the presence of different levels of 2,4-pentanedione is shown in Figure 12. The catalyst level in the formulation for DBTDL is 0.0042 % Sn on resin and for AlCh1 is 0.052 % Al on resin. The level of 2,4-pentanedione was 0, 0.58, 1.23 and 1.8% on resin solids or a molar ratio of tin to pentanedione 0, 163, 345 and 505; for the aluminum chelate the ratio was 0, 3, 6.4 and 9.3. The same experiment was also conducted for the bismuth catalyst and no increase in potlife was observed.

The relative rate of reaction of n-butyl isocyanate with 2-ethylhexanol and water was measured by FT-IR in a THF solution using DBTDL and ZIRC A catalyst. The IR shows a clear reduction in urea formation with the ZIRC A catalyst compared to DBTDL (Figure 13).

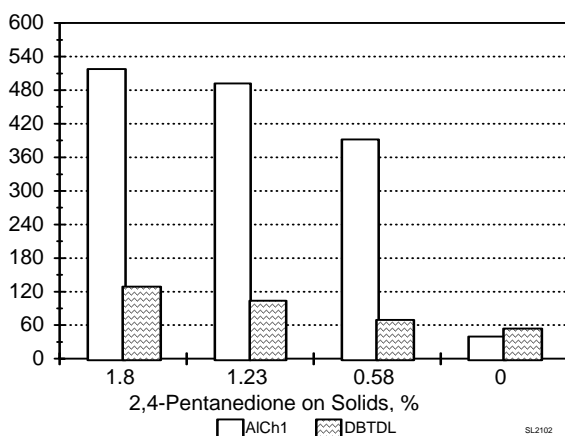


Figure 12. Time to reach double viscosity for a DBTDL and AlCh1 catalyzed formulation, in the presence of 2,4-pentanedione. Temperature 25°C.

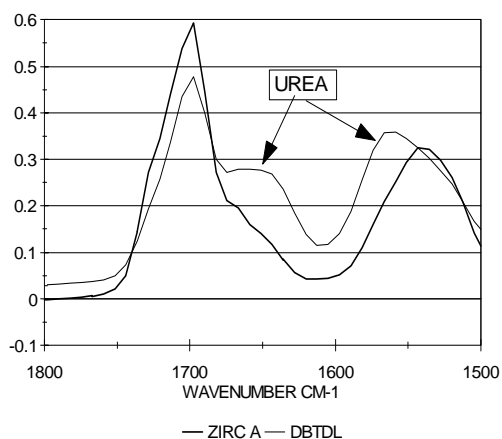


Figure 13. FT-IR spectrum. Absorbance of reaction product butyl isocyanate, 2-ethylhexanol and water molar ratio 1/1/2. Metal 0.01 %

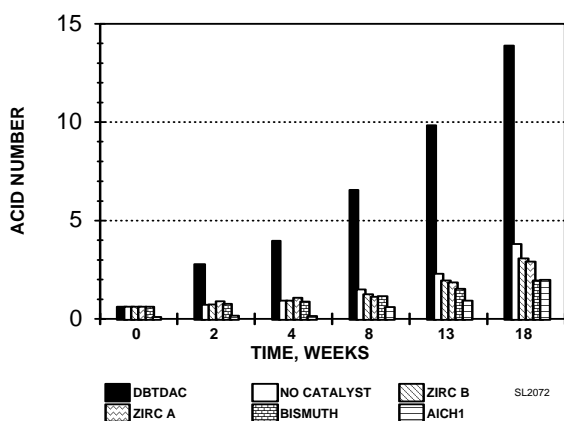


Figure 14. Hydrolysis of polyester resin in the presence of catalyst. Metal 0.1 %

The effect of catalysts on the hydrolysis of a polyester resin was measured in a 90 % homogenous solution of a low molecular weight polyester resin in a water/methylethylketone blend at a 1/3 ratio. This corresponds to a ratio of water to ester groups of 1.5 to 1. The test was conducted at 50°C for 18 weeks (3000 hours). After this time the acid number of the solution was measured. The polyester had an acid number of less than 0.1 at the start of the test. The pH of the solution was slightly acidic, no adjustments were made during the test (Figure 14).

A water-borne two component isocyanate crosslinked coating was formulated with a commercially available water-dispersed resin²² and a HDI-trimer. The ratio of NCO to OH used was 1.3. The formulation was tested uncatalyzed, catalyzed with DBTDL (0.0074 % Sn on resin solids) and with ZIRC B (0.008 % Zr on resin solids).

Table 1 Cure Response of Water-borne Two Component Coating

Formulation

COMPONENTS

Part A Resin component

	<u>Weight, %</u>	<u>Weight, %</u>
Polyester polyol (70 % solids in water)	41.3	41.3
Water deionized (1)	9.3	9.3
Flow and leveling agent	0.17	0.17
Dibutyltin dilaurate (DBTL)	0.04	-----

Part B_(isocyanate/OH ratio 1.3/1)

Polyisocyanate HDI-trimer	38.1	38.1
ZIRC B diluted with a reactive diluent	-----	1.34
Water deionized (2)	<u>11.2</u>	<u>9.8</u>
Total	100.0	100.0

Components A and B were mixed on a high speed agitator and blended with the water (2).

Film Properties Drying conditions 25°C, 50-60 % relative humidity.

Catalyst on Resin Solids	<u>No catalyst</u>	<u>DBTDL</u>	<u>ZIRC B</u>
Zirconium, %	-----	-----	0.008
Tin, %	-----	0.0075	-----
Aged before application, hours	0	0	0
Paint appearance	foam	foam	no foam
Film properties			
Tack free (hours)	5	3.5	3.75
Through dry (hours)	8	4.5	4.0
Gloss, 20°, %	53.0	94.7	94.9
Gloss, 60°, %	84.7	99.7	99.9

Catalyst on Resin Solids	<u>No catalyst</u>	<u>DBTDL</u>	<u>ZIRC B</u>
Aged before application, hours	1	1	2
Paint appearance	foam	1 hour gel	no foam
Film properties			
Gloss, 20°, %	75.0		88.3
Gloss, 60°, %	92.4		97.8

Aged before application, hours			4
Paint appearance			foam
Film properties			
Gloss, 20°, %			87.4
Gloss, 60°, %			96.2
Maximum potlife (hours)			3 hours no foam

The appearance of the coating from above formulation can be seen in Figure 15. The DBTDL catalyzed formulation was applied after ½ and hour, the ZIRC B formulation after mixing and after 2 and 4 hours. DBTDL shows gassing in the film and poor flow after only ½ hour and gelled at 1 hour. The ZIRC B formulation is stable for at least 4 hours. The relative humidity during the application was 50-60 % and the temperature was between 20-25°C. Figure 16 shows the film appearance at 50 and 70 % humidity for ZIRC B and for DBTDL at 70 % RH. The DBTDL catalyzed films lose considerable gloss under the 70 % humidity conditions. The ZIRC B catalyzed film retains almost all the gloss at 70 % RH. At 90 % RH all films are essentially flat.



Figure 15. Film appearance of water-borne two component coating, film thickness 25 η. Cure conditions room temperature and relative humidity 50-60%. Catalyst ZIRC B and DBTDL.



Figure 16. Film appearance water-borne two component coating, film thickness 25 η. Cure conditions, room temperature and relative humidity 50 and 70 %, ZIRC B and DBTDL catalyst.

In an attempt to better understand the mechanism of the $\text{Zr}(\text{AcAc})_4$ catalysis of the isocyanate/hydroxyl reaction several NMR experiments were conducted with model compounds. The initial experiments were aimed at determining the extent of interaction of the isocyanate and hydroxyl with the metal complex.

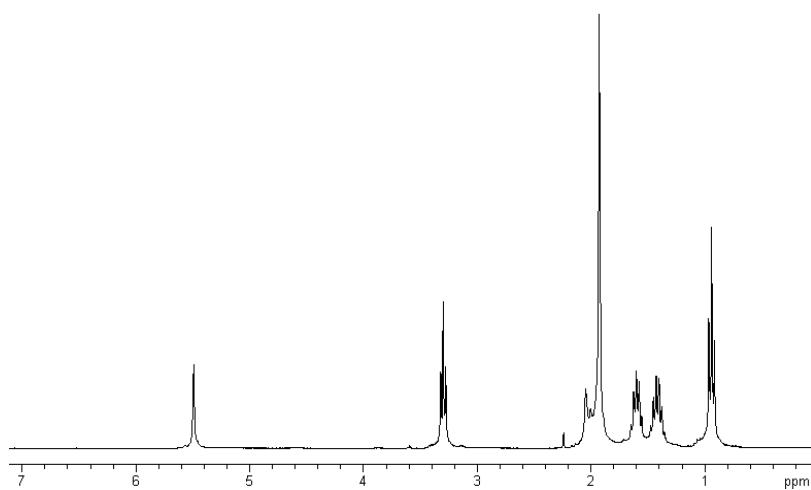


Figure 17. $\text{Zr}(\text{AcAc})_4$ + 3 eq. n-butyl isocyanate in CDCl_3 solution at 25 °C

Addition of n-butyl isocyanate to a solution of $\text{Zr}(\text{AcAc})_4$ in CDCl_3 at room temperature showed no broadening of any of the resonance associated with either the metal complex or the isocyanate. The results are shown in Figure 17. This indicates that there is relatively little, if any, interaction between the isocyanate and the $\text{Zr}(\text{AcAc})_4$.

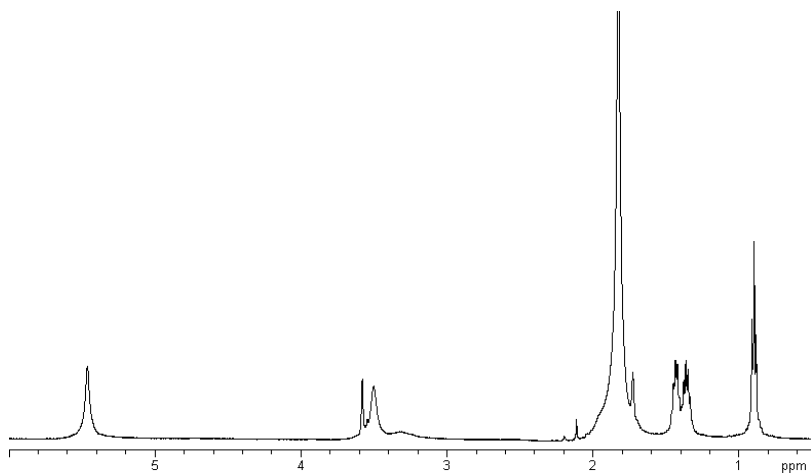


Figure 18. $\text{Zr}(\text{AcAc})_4$ + 3 eq. n-butanol in d_8 -THF at 25 °C

In contrast, addition of n-butanol to a d_8 -THF solution of $\text{Zr}(\text{AcAc})_4$ at room temperature results in broadening of all resonances of both the ligand and n-butanol in the ^1H -NMR spectrum.

When the sample is cooled to $-50\text{ }^\circ\text{C}$ the resonances for both the $\text{Zr}(\text{AcAc})_4$ and alcohol sharpen to their normal peak widths and two separate types of n-butanol are observed.

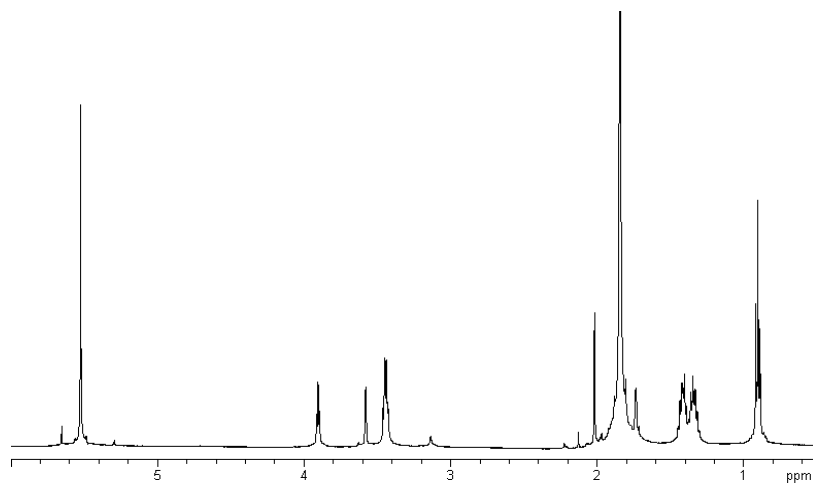


Figure 19. $\text{Zr}(\text{AcAc})_4 + 3 \text{ eq. n-butanol}$ in $\text{d}_8\text{-THF}$ at -50°C

However, there was no evidence in the ^1H NMR spectrum at low temperature of a Zr-H bond. The rate of exchange of the n-butanol into the complex could be determined from the temperature dependence of the line widths.

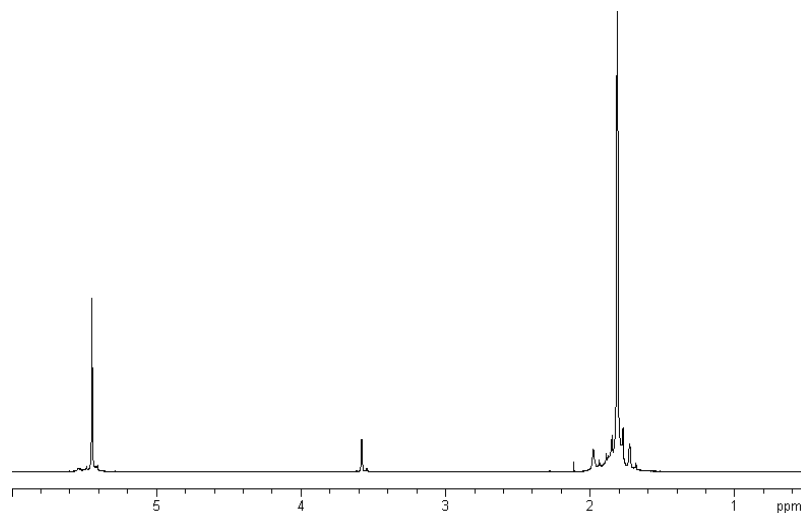


Figure 20. $\text{Zr}(\text{AcAc})_4$ in $\text{d}_8\text{-THF}$ at 25°C

Comparison of the room temperature ^1H spectrum of $\text{Zr}(\text{AcAc})_4$ (Figure 20) and n-butanol (Figure 21) with that of the corresponding spectrum at room temperature where n-butanol has been added shows that the presence of additional n-butanol causes significant broadening of all peaks. We also attempted to conduct a similar experiment with water instead of n-butanol. It was not possible to draw any

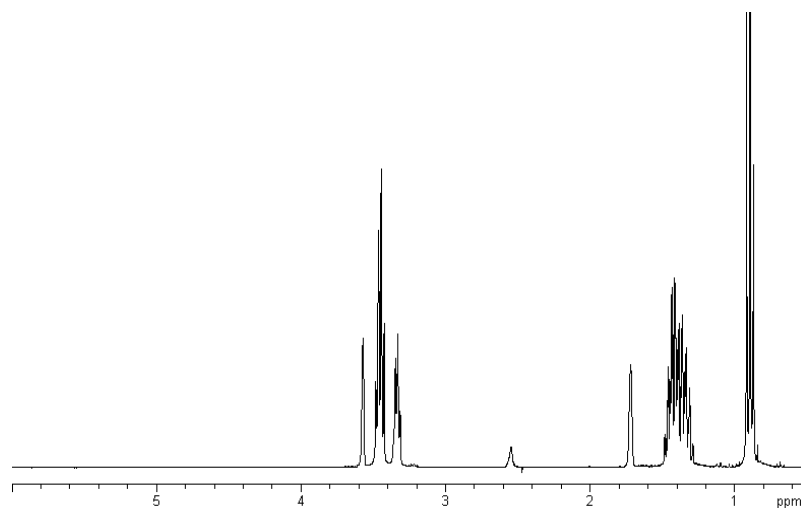


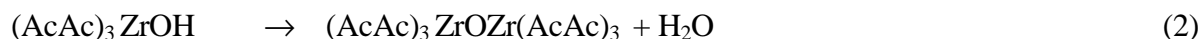
Figure 21. n-butanol in $\text{d}_8\text{-THF}$ at 25°C

conclusion from this experiment because of hydrolysis of the zirconium complex.

DISCUSSION AND CONCLUSIONS

Catalysis with Metal Salts and with Metal Complexes

Many metal salts and chelates can catalyze the reaction of polyisocyanates with hydroxyl compounds (Figure 1). Some metals (Zn, Co, Ni, Cr) show no change in catalytic activity between the carboxylate salt and the dionate complex. For zirconium and aluminum only the dionate complex was catalytically active. On an equal metal basis ZrAcAc is about 3-5 times more active as a catalyst than DBTDA in reducing the gel time (Figure 2). Aluminum dionate complexes on the other hand are substantially less active as catalysts. Tack-free time of the ZrAcAc catalyzed formulation is about three times longer than with DBTDL. This observation indicates that some deactivation of the ZrAcAc complex is taking place in thin films. Based on the poor solubility of the ZrAcAc complex in most solvents and the potential for hydrolysis with water we ran additional experiments where we added free 2,4-pentanedione to the formulation. Not only is 2,4-pentanedione an excellent solvent, it also should reduce any hydrolysis of the ZrAcAc complex. As shown in Figure 3 increasing the ratio of 2,4-pentanedione to zirconium from 4 to 376 decreases the potlife from 45 to 22 minutes and at the higher ratio of 748 and 1347 increases the potlife to 32 and 54 minutes respectively. The tack free time decreases as the ratio of pentanedione is increased from 15 hours to 7, 5, 3 hours respectively. Increase in potlife of DBTDL catalyzed formulations on addition with 2,4-pentanedione is known and is practiced widely in high solids coatings. The rather erratic behavior of zirconium cannot be explained by a single mechanism. Hydrolysis of the zirconium catalyst according to equation (1) and polymerization to a polymeric form (eq. 2) could cause a reduction in reaction rate²³. We had noticed in a separate study a lower reaction rate of Zr-dionate complexes with a substitution of <4. Increasing the amount of free pentanedione would inhibit the effect of any water on the zirconium complex. (eq. 2). Further increases in the ratio of pentanedione could inhibit the exchange reaction of the Zr(AcAc)₄ complex with the alcohol.



Ligands for Zirconium

As shown in Figure 4 only dionate complexes with alkyl substitution at the 1 and 5 carbon are effective catalysts. Substitution at the 3 carbon reduces the activity as does substitution with either aromatic or fluoro groups. Also acetoacetate groups do not produce an effective catalyst. It appears both steric and electronic influences affect the catalytic activity of this complex.

Formulations

Gel times are shown for an acrylic HDI-trimer system for ZIRC B, ZIRC A and DBTDL in Figure 6. The ZIRC B catalyst gives the shortest gel time, ZIRC A because of the excess 2,4-pentanedione give improved gel times. Figure 7 shows the gel time for Bi oct. and AlCh1 catalyst. Bi oct. on a metal basis is similar in activity to DBTDL, whereas for the aluminum chelate compound about 10 times the metal content is required to match the cure performance. The tack-free time achieved with ZIRC A and B is of the same order of magnitude, both catalysts are about 4-8 times faster than DBTDL (Figure 8). Evaporation of 2,4-pentanedione can explain the comparative higher reaction rate in films than shown in the gel test for the ZIRC A catalyst.

Both Bi oct. and AlCh1 behave similarly in the tack-free test as already shown in the gel test. (Figure 9).

Dry-trough times for both ZIRC A and ZIRC B are about equal and approximately at an equal metal level four times faster than for DBTDL. On a comparative basis, the dry-through times for Bi oct. and DBTDL are substantially slower but still acceptable for many applications. In subsequent experiments it was determined that the cure response of the Bi oct. catalyst could be substantially enhanced by choosing a less polar solvent. Bi oct. demands a rather non-polar environment to assure good catalytic activity. This exceptionally fast reaction with ZIRC B suggests that this catalyst can be used in plural component spray applications where mixing of the isocyanate and the polyol takes place at the gun. Other applications are in the RIM area.

Potlife of the Formulation

For many applications batch mixing of the polyol and the polyisocyanate crosslinker is used in which case a reasonable potlife is required. In low solids coatings it is possible to achieve an acceptable potlife by using a lower functionality resin and a rather slow reaction system. Because of the lower concentration of functional groups at a low nonvolatile content the reaction rates in solution are rather slow. Upon solvent evaporation increase in the concentration of functional groups accelerates the reaction rates. Because of the much higher molecular weight of the polymers used in low solids coatings only a low conversion of hydroxyl-isocyanate groups is required to build a sufficient crosslinked network to achieve a tack-free surface or dry through.

In high solids coatings the concentration of functional groups in solution and in the film are very similar, we therefore cannot rely on a change in concentration to effect potlife and reactivity. Because of the lower molecular weight and also lower functionality of high solids coatings we also require higher conversions of functional groups to achieve tack-free and dry-through conditions.

Addition of excess 2,4-pentanedione can improve the potlife as seen with ZIRC A catalyst. Further improvements in potlife can be achieved with aluminum chelate (Alch1). Compared to DBTDL the potlife of a formulation can be substantially enhanced by addition of 2,4-pentanedione²⁴. Both formulations were adjusted for an equal dry-through time of about 50 minutes (Figure 12).

Relative Reaction Rates Hydroxyl-Water

As shown in Figure 13, n-butyl isocyanate preferentially reacts with the hydroxyl groups instead of water and the formation of polyureas is minimized in the presence of ZIRC A compared to DBTDL. This selectivity of the isocyanate-hydroxyl reaction is not only of importance in the evolving market for two component water-borne isocyanate crosslinked coatings, but also in many high solids coatings. Blushing of high solids coatings at high humidity or even gassing is an often encountered problem with high solids isocyanate crosslinked coatings.

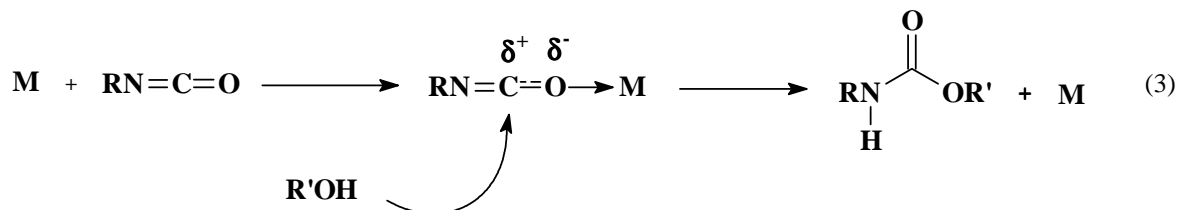
Hydrolysis of ester group containing resins in the presence of dialkyltin catalysts is a problem for many polyester-urethane polymers on exposure to water. We have demonstrated that DBTDA and presumably, DBTDL, are very effective catalysts in increasing the hydrolysis of a polyester resin. Zirconium, aluminum chelate and also bismuth salts do not catalyze the hydrolysis reaction. This would indicate that these catalysts can give improved resistance properties and also suggests their use in the preparation of polyurethane polymers.

Because of the growing importance of water-borne two component coatings we also investigated the use of a ZIRC B catalyst, since DBTDL gives very fast water reaction rates. In a high solids waterborne polyester/polyisocyanate coating a potlife of only 30 minutes is achieved with

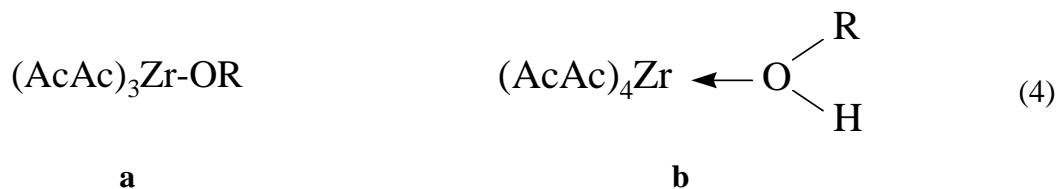
DBTDL and almost immediate gassing due to carbon dioxide development is observed. Even the uncatalyzed formulation has a tendency to foam. Even after 4 hours the ZIRC B catalyst gave acceptable films (Table 1). The appearance of the films is shown in Figure 15 and 16. In both formulations the catalyst levels were adjusted for equal tack-free and dry-through time. For the ZIRC B catalyst good gloss is obtained even after a potlife of 4 hours. Some decrease in flow and leveling is noticed and there is some formation of carbon dioxide bubbles. Although the gloss is still excellent for the DBTDL catalyzed formulation after a 30 minute potlife it is difficult to form a film wherein no CO₂ bubbles are included. Increasing the humidity from the normal relative humidity of 50-60 % to 70 % causes the ZIRC B catalyzed formulation to lose some gloss, while DBTDL catalyzed films show even lower gloss (Figure 16). We have also prepared films at 90 % humidity, these films were flat and milky in appearance. This indicates that for ZIRC B we have a cure window in regard to relative humidity which in the upper range is approximately 70 %.

Mechanism of Catalysis with Zirconium Chelate Catalyst

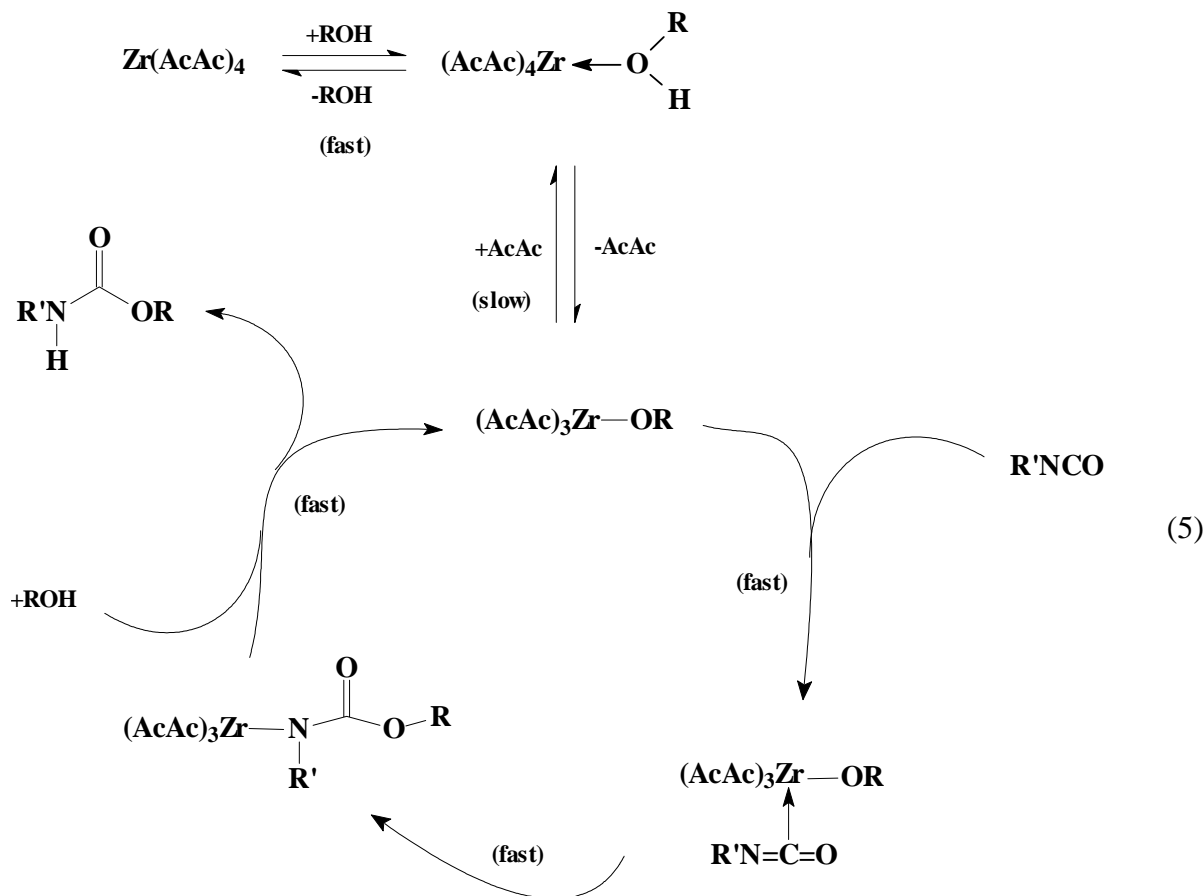
The generally accepted mechanism proposed for the DBTDL catalyzed reaction of isocyanate and hydroxyl can be viewed as a Lewis acid type mechanism involving polarization of the carbonyl by the metal complex followed by nucleophilic attack of the hydroxyl (Eq. 3).



All of the ¹H NMR evidence for Zr(AcAc)₄ reported above suggests a mechanism which is significantly different from the standard Lewis-acid type mechanism. With the Zr(AcAc)₄/isocyanate/hydroxyl system, we postulate that the first step of the reaction involves the coordination of the alcohol to the metal center. Two possible types of coordination/activation are shown in (Eq. 4).



The NMR evidence favors structure b, an independent series of ¹H NMR experiments showed that the rate of exchange of deuterium from n-BuOD into the AcAc ligands of the Zr(AcAc)₄ is slow relative to the rate of the ligand exchange process. A reasonable mechanism is shown in Eq. 5. The (AcAc)₃ZrOR alcoholate formed reacts with the isocyanate forming an insertion complex, which in the presence of alcohol forms the urethane and returns the alcoholate into the reaction sequence.



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