Influence of the Catalyst on the Kinetics of a RIM Formulation

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Synopsis

The influence of three different catalysts [triethylendiamine (TD), stannous octoate (SO), and dibutylindilaurate (DBTDL)] and their blends (TD + SO and TD + DBTDL) on the kinetics of a RIM formulation, based on a high functionality polyether–polyol and a polymeric MDI, has been studied using the adiabatic temperature rise method and Fourier transform infrared spectroscopy. The synergism observed in the DBTDL/TD systems is explained by means of complex formation between the amine-based and metal-based catalysts. Infrared spectroscopy data support this complex formation. The SO/TD systems do not exhibit synergetic behaviour, being the reaction rate controlled by the metal catalyst which complexes the isocyanate group.

INTRODUCTION

The reaction injection molding (RIM) process implies the filling of a mold with a highly reactive system (gel time ranging between 2 and 10 s). Thus, the formulation must be designed to account for two competitive events: flow across the mold and reaction of the components (which gives rise to a viscosity increase and a flow capability decrease). It is clear from the above mentioned that the role played by the catalysts in polyurethane RIM formulations is essential. Moreover, the catalytic system brings about faster reactions and curings, establishes a proper balance between propagation reaction and foaming process, and influences the properties of the final part. Modeling the thermoset process requires[1] the knowledge of reaction kinetics, reaction energetics $[\Delta H, C_p(T, c)]$ and the relation between viscosity and reaction extent. The first of these requirements has been fulfilled in this work using the adiabatic reactor method.

The catalytic system used in the PU (polyurethane) RIM process involves a series of acid–base equilibria characterized by complex formation between the catalyst and the raw materials. Although in the PU literature the catalyst influence is a very well-studied subject,[2-6] very few studies deal with the synergism behavior observed when blends of amine-based and metal-based catalyst are used together.[5] Herein, an attempt to determine the degree of influence of catalyst blends has been carried out.

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The aim of this work is to study the influence of the catalytic system on the reaction kinetics of a rigid polyurethane formulation. In order to fulfill this objective, two types of systems have been studied:

1. *Systems with one catalyst:* In this case the influence of the nature of the catalyst (acid–base), the covalency and the concentration is reported.
2. *Systems with two catalysts:* Blends of the amine-based catalyst with the two metal compounds will allow us to determine the synergism level and the influence of covalency and composition.

In order to deepen in the complex formation mechanism, infrared spectroscopy measurements have been carried out.

EXPERIMENTAL

The components used for carrying out the present study were a polymeric MDI [Suprasec VM30; %NCO equal to 29 (ASTM D1638-74)] and a polyether-polyol [Daltocal P140; hydroxyl number equal to 490 (ASTM D2849-69); average functionality equal to 4.8] provided by ICI. The catalysts employed were tin octoate (SO), dibutyltindilaurate (DBTDL), and triethylene diamine (TD) all of them from Ciba-Geigy.

Adiabatic Reactor Method

The reaction kinetics were followed by monitoring the adiabatic temperature change as a function of time. This method has been reported to be most convenient for fast bulk polymerizing systems.[7-12] The data analysis has been carried out using[12]

$$\ln K = \ln\left((dT/dt)/\left\{\Delta T_{ad}[1 - (T - T_0)/\Delta T_{ad}]^{n}\right\}\right)$$

$$= \ln A - E_A/RT_{exp} \tag{1}$$

where K is the overall rate constant, n the reaction order, T_{exp} the experimental temperature, T the adiabatic temperature (obtained correcting the experimental temperature by means of the heat lost factor), $\Delta T_{ad} = (-\Delta H)/C_p$, $-\Delta H$ being the heat evolved per unit mass and C_p the specific heat (considered herein as constants although this is not a compulsory condition), T_0 the room temperature, A the Arrhenius preexponential factor, and E_A the reaction activation energy.

The reactor was a glass tube of 115 mm length and 23 mm diameter insulated using closed cell polystyrene foam (Dow Chemical) in order to get the adiabatic conditions. An iron-constantan thermocouple was used in order to measure the adiabatic temperature rise which was monitored through an IBM computer.

The stoichiometric amounts of temperated components were poured onto the reactor together with the catalytic system and the whole was whipped by means of a two propellers motor mixer.

Infrared Spectroscopy

A Mattson Instruments Fourier transform infrared spectrophotometer (Model Polaris Icon) has been used. All the measurements have been carried out at 298 K. The maximum resolution was set at 4 cm^{-1} and the number of scans used was 256.

Model samples were prepared by mixing the two catalysts in n-propanol [molar ratio 1 (total amount of catalyst): 5] varying the molar composition of both of them. The infrared sample preparation was carried out by means of dried martered KBr pellets. A pellet of around 200 mg of KBr and 3–6 mg of problem sample was made in a stainless steel microdie. Sample compartment was carefully dried by means of a dry air installation in order to remove as much humidity as possible.

The infrared study has been focused in the spectral region 1500–1750 cm^{-1} where the C$=$O stretching vibration and the COO$-$ stretching asymmetric vibration are localized. The vibration placed at 1600 cm^{-1} is related to the COO$-$ bonded to the tin atom, while the other one placed at 1565 cm^{-1} is related to the dissociated carboxylate anion as separated in ion pairs (these data correspond to the DBTDL catalyst[13]).

RESULTS AND DISCUSSION

As has formerly been pointed out in this paper, the aim of this work is to determine the catalytic influence of amine-based and metal-based catalysts on the kinetics of a RIM formulation based on a high functionality polyether–polyol and a polymeric MDI.

Single Catalyst Systems

Figure 1 shows the behavior associated with the individual catalysts which fits the literature results.[1] As can be seen from this figure, the catalytic activity is higher for the metal-based catalysts than for the amine-based one and, between the two tin compounds, this activity decreases with increasing tin covalency. The representation of log $t_{1/2}$ vs. logarithm of molar catalyst concentration is found to follow a linear dependency. The exponential forms of these experimental relationships valid in the measured concentration range are:

1. TD: $\quad t_{1/2} = 21.73\,[\mathrm{TD}]^{0.94}, 1.46 \times 10^{-2} \le [TD] \le 7 \times 10^{-2}$ mol/L

$$(2)$$

2. $DBTDL$: $t_{1/2} = 15.28\,[\mathrm{BD}]^{0.5}, 3.9 \times 10^{-3} \le [DB] \le 2.7 \times 10^{-2}$ mol/L

$$(3)$$

3. SO: $\quad t_{1/2} = 2197.86\,[\mathrm{SO}]^{1.5}, 7.8 \times 10^{-3} \le [SO] \le 3 \times 10^{-2}$ mol/L

$$(4)$$

The behavior associated with the amine catalyst can be explained on the basis of Farkas and Stromm[3] mechanism. The reaction takes place by interaction of
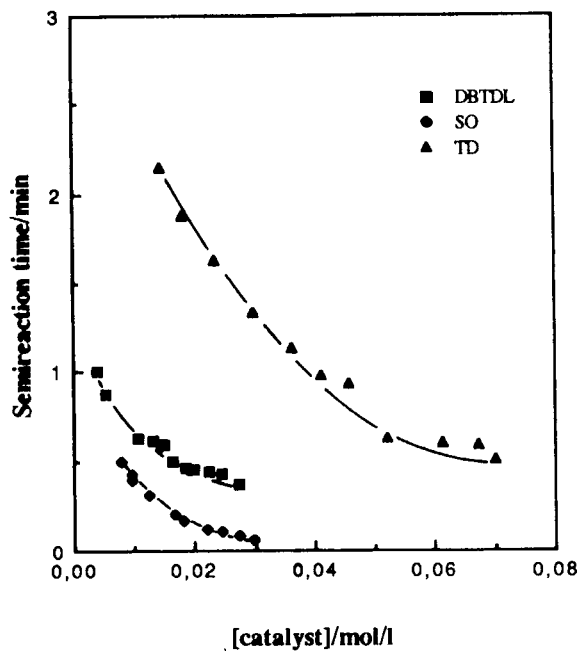
Fig. 1. Semireaction time as a function of catalyst concentration for the systems with only one catalyst.

the isocyanate with a polarized amine–alcohol complex (see Ref. 13). With respect to metal catalyst they are said to operate via ligand exchange at the central tin atom.[13]

Wongkamolsesh and Kresta[13] in their study about the catalytic activity of DBTDL on model systems isocyanate/n-butanol concluded that the hydroxyl group of the alcohol solvates the tin central ion, causing the separation of the carboxylate anion to take place. This solvation enables the formation of a complex between the tin ion and the isocyanate. It is important to note that they did not find any coordination between isocyanate and DBTDL. These results were, moreover, confirmed by conductivity measurements.

In order to clarify the differences between both metal catalysts, Fourier transform infrared (FTIR) studies have been carried out. FTIR spectroscopy will provide us a better understanding of the type of acid–base equilibria which takes place in the poliol side tank during RIM processing. The real behavior has been simulated herein using n-propanol instead of the polyfunctional polyol for easier sample handling.

Figures 2, 3, and 4 show the spectra of the single catalyst in n-propanol (Fig. 2, DBTDL; Fig. 3, SO) and in MDI (Fig. 4, SO). The spectrum of DBTDL in MDI has not been obtained because it has already been made by Wongkamolsesh and Kresta,[13] who did not find any outstanding change in the DBTDL spectrum or in the MDI one. It is worthwhile to point out from these figures that:

1. The concentration of dissociated carboxylate, for the DBTDL catalyst, increases in the presence of the alcohol (Fig. 2)
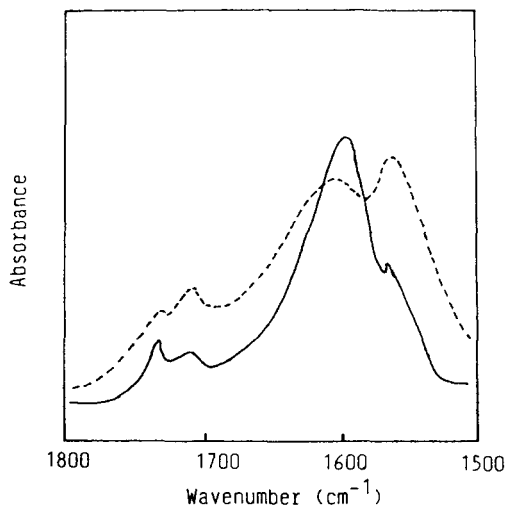
Fig. 2. Infrared spectra of neat DBTDL (—) and DBTDL in *n*-propanol (molar ratio 5 : 1) (---).

2. The neat SO spectrum does not display any peak at 1600 and 1565 cm^{-1}, but at 1612 and 1554 cm^{-1}. The addition of the alcohol shifts the 1612 peak to 1605 cm^{-1} and change the intensity of this spike, while the 1554 cm^{-1} peak becomes smaller (Fig. 3)

3. The addition of the MDI to SO (Fig. 4) brings about three major changes:

- The 1612 and 1553 cm^{-1} peaks shift to lower wavenumbers up to 1600 and 1544 cm^{-1}, respectively. The intensities of both spikes stay practically unaffected

- The C=O asymmetric stretching vibration associated with one of the blended compounds shifts towards lower wavenumbers going from 1728 to 1650 cm^{-1}
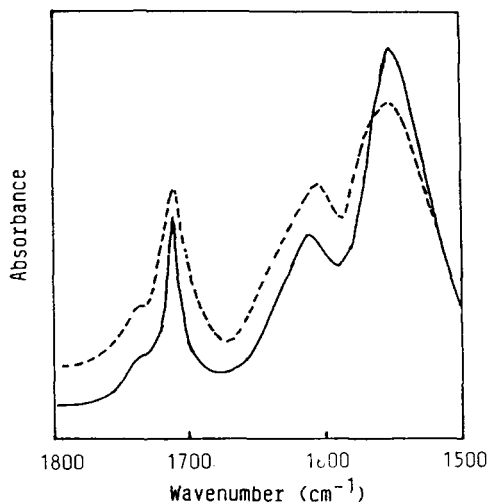

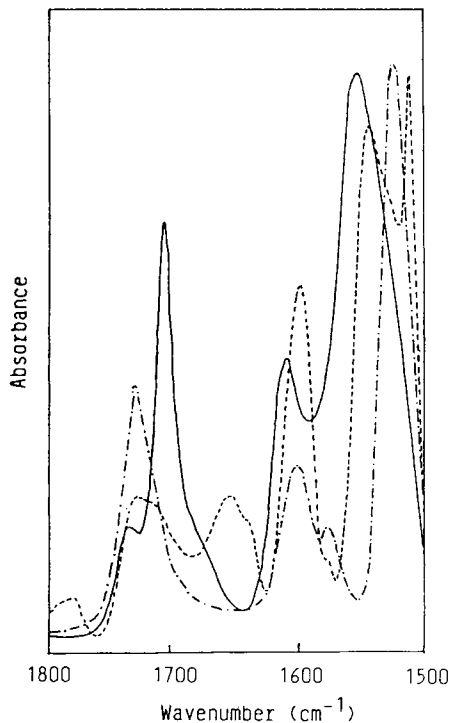Fig. 3. Infrared spectra of neat SO (—) and SO in *n*-propanol (molar ratio 5 : 1) (---).

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Fig. 4. Infrared spectra of neat SO (—), neat MDI (– · – ·), and SO/MDI (molar ratio 5 : 1) (---).

- The absorption associated with the vibration of the aromatic groups of the MDI molecule placed at 1524 cm^{-1} shifts towards lower wavenumbers (1512 cm^{-1}) in the presence of the metal catalyst SO

The characteristic isocyanate band (2278 cm^{-1}) remains unaffected.

Accounting for the similarity of our results with those by Wongkamolsesh et al.[13] for the DBTDL catalyst, the experimental findings for the RIM formulation when this catalyst is used can be explained on the basis of the mechanism proposed by these authors. The case of the SO catalyst is, however, very different. The FTIR results for this catalyst enable us to suggest that:

1. The addition of n-propanol promotes the bonding of carboxylates to tin (the ratio between 1605 and 1554 cm^{-1} peaks increases
2. The presence of isocyanate yields the formation of a complex isocyanate/catalyst (when both are mixed, a yellow precipitate is formed) which increases the electrophylicity of the isocyanate carbon atom

These statements find explanation in the change of inductive and resonance effects when the alcohol or the isocyanate are added to the catalyst. The tin atom in the SO catalyst is more electronegative than the tin in the DBTDL catalyst due to the existence of empty "P" orbitals in the tin (II) atom. This

more electronegative character of the tin(II) can give rise to an increase in the stretching frequency of the bonded carboxylates due to inductive effects.

The addition of the alcohol shifts the bonded carboxylates vibration absorption towards lower wavenumbers as a consequence of alcohol/catalyst interactions which reduce the inductive effect within the catalyst. However, the solvation effect, which increases the concentration of dissociated carboxylate in the DBTDL case, does not have a great effect in the SO catalyst. On the other hand, the addition of MDI to the catalyst brings about important changes in the absorption spectrum which suggest the coordination of the isocyanate with the tin(II) ion via the lone-pair electron system of the nitrogen atom of the isocyanate group. This adduct formation will give rise to an increase of the resonance effect within the isocyanate group and a decrease of the carbonyl vibration frequency.[14] The downward of the aromatic group vibration corroborates this supposition.

Summing up, it can be concluded that whereas in DBTDL-catalyzed systems the alcohol solvates the tin(IV) ion prior to isocyanate/catalyst com-
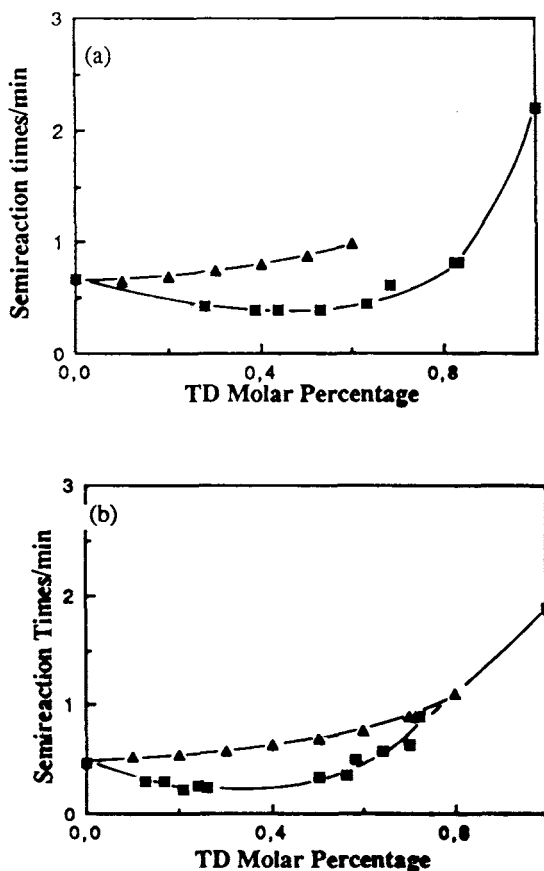

Fig. 5. Semireaction time as a function of TD molar percentage for the DBTDL/TD system: (a) $C_T = 1.1 \times 10^{-2}$ mol/L; (b) $C_T = 1.8 \times 10^{-2}$ mol/L; (■) experimental values; (▲) calculated values via eq. (3).

plexation, the SO-catalyzed systems show reaction through the direct forma-
tion of such a complex.

The application of eq. (1) shows that the best fitting occurs for reaction
orders of approximately 2. This second-order behavior agrees with several
mechanisms reported in the subject literature.[2,4,12] Once the reaction order
has been determined, the activation energy associated with the process can be
calculated by means of the Arrhenius equation. The mean activation energies
obtained are

- systems catalyzed by DBTDL: 60 kJ/mol
- systems catalyzed by SO: 77 kJ/mol
- systems catalyzed by TD: 38 kJ/mol

Two Catalysts Systems

The study of the kinetics of this RIM formulation when a blend of catalysts
is used is a difficult task due to the complexity arising from the existence of
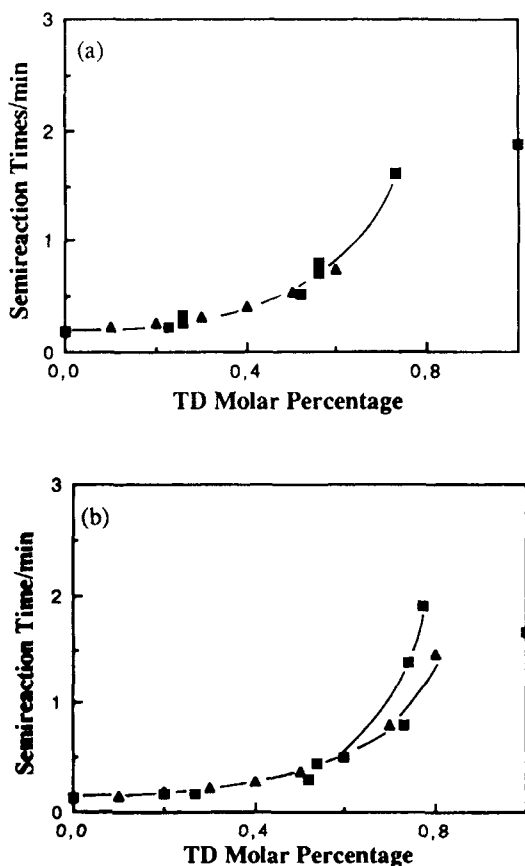different kind of reactions within the system (e.g., uncatalyzed reaction,

Fig. 6. Semireaction times as a function of TD molar percentage for the SO/TD systems:
(a) $C_T = 1.8 \times 10^{-2}$ mol/L; (b) $C_T = 2.3 \times 10^{-2}$ mol/L; (■) experimental values; (▲) calculated
values via eq. (4).

metal-catalyzed reaction, amine-catalyzed reaction, amine/metal complex cat-
alyzed reaction, side reactions, ...). The main aim of this study is to
determine the influence of the catalyst ratio, total catalyst concentration, and
the type of metal catalyst on the kinetics of the system under study.

Figures 5 and 6 display the semireaction times as a function of TD molar
percentage for the two different metal catalysts and two distinct total catalyst
concentrations. Although the reaction orders with respect to the catalysts are
an unknown parameter, we can make use of eqs. (3) and (4) in order to
compare the semireaction times associated with the neat catalyst systems and
those associated with blended catalyst systems. It is evident from these
figures that:

1. The semireaction times found for the DBTDL/TD systems are lower than
   those corresponding to the neat DBTDL, independently of catalyst concen-
   tration
2. The experimental semireaction times obtained for the SO/TD systems fit
   the relationship given by eq. (4) in the concentration range where this
   equation finds application

As in the case of single catalyst systems, infrared studies have been carried
out in order to determine possible changes in the vibration modes depending
on the variables under study. The spectra obtained for the blended catalyst in
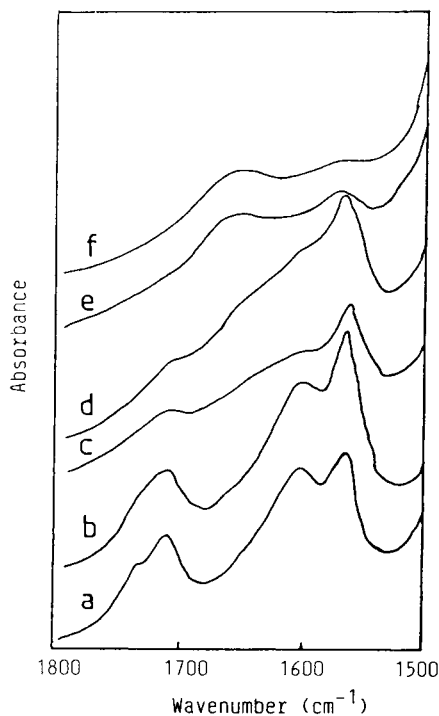n-propanol as a function of TD molar percentage are shown in Figures 7 and

Fig. 7.   Infrared spectra of the DBTDL/TD/n-propanol system (TD molar composition: (a) 0;
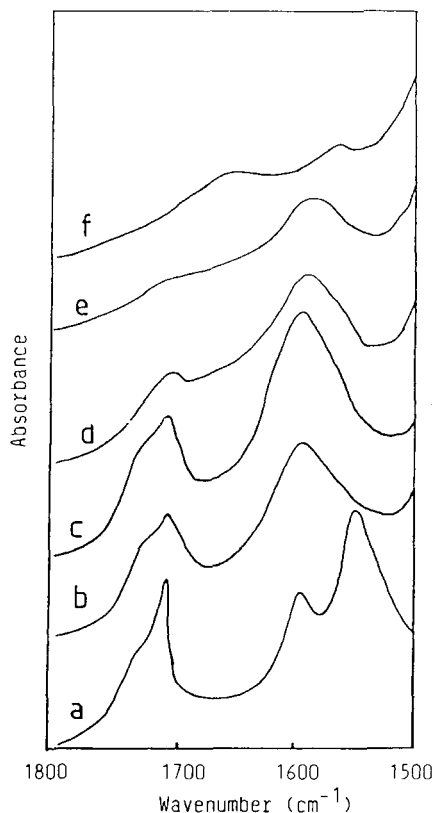(b) 0.1; (c) 0.3; (d) 0.5; (e) 0.7; (f) 0.9.

Fig. 8.   Infrared spectra of the SO/TD/n-propanol system (TD molar composition): (a) 0; (b) 0.1; (c) 0.3; (d) 0.5; (e) 0.7; (f) 0.9.

8. It is evident from these figures that:

1. The presence of the amine catalyst in DBTDL systems brings about an increase of the absorbance of the 1565 cm^{-1} spike which implies that the free carboxylate concentration increases.
2. The presence of the amine-based catalyst when the organometal catalyst is SO yields the disappearance of the 1554 cm^{-1} peak and the appearance of a unique spike placed at 1594 cm^{-1}.

These two observations together with the semireaction times data enable us to establish the possible mechanism which takes place depending on the organometal catalyst.

In the case of DBTDL/TD systems and accounting for the stronger basic character of the amine catalyst compared with the isocyanate and the alcohol, it is expected the formation of an octahedric complex with one of the complexation sites occupied by the NR_3 catalyst (which donors its free electron pair) and the other one free for the activated complex formation with the isocyanate or the alcohol (the infrared studies show that the addition of the amine catalyst to the model solution leads to a decrease of the metal
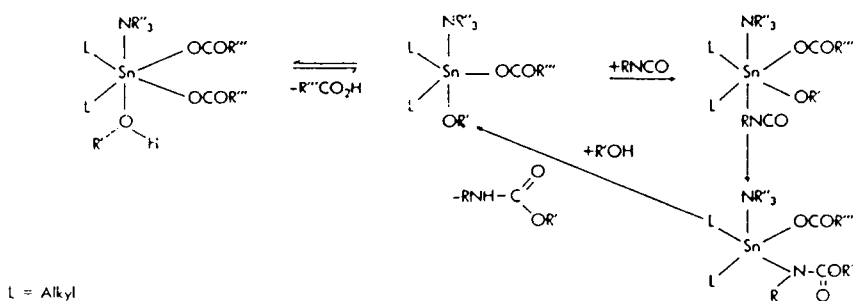
Fig. 9. Possible reaction mechanism for the systems DBTDL/TD.

bonded carboxylate concentration). One possible mechanism is shown in Figure 9.

After formation of a tin alkoxide, one of the carboxylates takes over the alcohol proton and leaves free one of the complexation sites. This free site is then occupied by an isocyanate group. In the following step, both the alkoxy and the isocyanate react changing the complex structure from octahedric to trigonal bipyramidal. One of the polyols transfers to the activated complex, giving rise to liberation of the carbamate and the formation of the structure II. This complex formation speeds up the polyurethane reaction. In any case, it should be kept in mind that together with this possible mechanism, other different reactions (each catalyst acts individually, combination of these separate catalysis, side reactions, ...) can take place, making the whole mechanism very complex.

With respect to the SO/TD systems, the infrared and adiabatic reactor evidences suggest that the presence of the amine catalyst does not increase the concentration of free carboxylates which can be related to the synergetic behavior (as it has been pointed out for DBTDL/TD systems). In fact, the addition of the amine-based catalyst brings about the bonding of the free carboxylates to the tin(II) ion (as can be deduced from the infrared spectra shown in Fig. 8). Only the strong complex formation between isocyanate and metal-based catalyst can explain that the reactivity of the SO/TD systems remains unaffected with respect to the single catalyst systems. The possible cooperation of the amine catalyst (via the Farkas[3] mechanism) seems not to be very important due to the good fitting between experimental and calculated values.

CONCLUSIONS

The most outstanding conclusions associated with this study are: (1) The semireaction time values exhibit a logarithmic dependence on the catalyst concentration in the measured concentration range; (2) the SO catalyst acts via strong complex formation with the isocyanate; (3) the blended catalyst systems based on DBTDL show synergetic behavior which can be explained via complex formation between both catalysts; (4) the systems SO/TD do not display synergism.

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