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Catalysis of the Formation of Urethanes

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Introduction

Although much research has been done during recent years on the catalysis of the preparation of polyurethanes, especially in regard to foam formation,[1-8] little work has been done to elucidate the mechanism of catalysis.

Baker[1,2] and others[3,4] have made extensive investigations of catalysis by tertiary amines. This work has well substantiated that amine catalysts activate the isocyanate functional group for reaction with an active hydrogen compound.

Recent work by Britain and Gemeinhardt[5] has shed some light on metal salt catalysis. They postulated that this type of catalysis could occur by either of the paths shown in Figure 1. Although this work did help to make

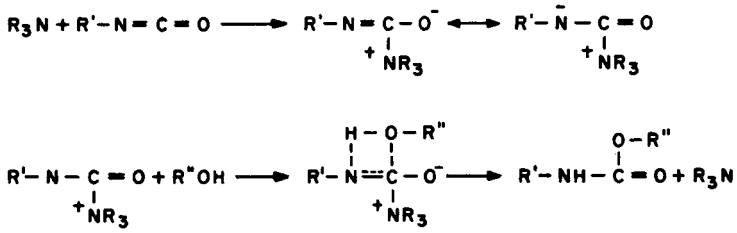

Fig. 1. Mechanism of amine catalysis.

metal salt catalysis more understandable from the standpoint that the salt activated the reagents by complexation, the postulated mechanism leaves something to be desired since it requires an attack by one electron difficient center on another. In addition, it was not shown (*1*) which of the two proposed modes of catalysis, if either, was preferred; (*2*) whether all metal salts catalyzed in the same manner; or (*3*) whether both types of catalysis went on simultaneously.

Therefore, the present investigation was conducted in an effort to answer these questions.

Experimental

To carry out this study, a variety of active hydrogen compounds, four catalysts, and two isocyanates were used. The active hydrogen compounds fell into two categories. The first consisted of the monofunctional com-

pounds, 1- and 2-butanol, 2-hydroxybutyl butyl ether (M-I), 1-ethyl-1-(2-hydroxybutyl)-2-butoxyethane (M-II), butyl-*N*-phenyl carbamate, and ethyl-*N*-ethyl carbamate. The second category consisted of the following polyfunctional compounds: a polyether polyol with secondary hydroxyl groups (P-I), a polyether polyol with 50% primary and 50% secondary hydroxyl groups (P-II), and an amine-based polyol with 50% primary and 50% secondary hydroxyl groups (P-III). The catalysts were triethylenediamine, stannous 2-ethylhexoate, cobaltous stearate, and the sodium salt of M-II. The isocyanates were phenyl isocyanate and tolylene diisocyanate (80/20 mixture of the 2,4- and 2,6-isomers).

Rate determinations were conducted as follows: A solution of 5 meq. of active hydrogen compound, 5 meq. of isocyanate, and 0.125 mmole of catalyst was made up in enough toluene to give a total volume of 100 ml. Aliquots of 6–7 ml. were taken from this solution and introduced into test tubes, which were immediately sealed. The sealed tubes were simultaneously immersed in the constant temperature bath and withdrawn at appropriate intervals starting with a "zero" sample after 3 min. of immersion. Rates were followed only to about 50–60% reaction so that linear curves would result even though groups with varying reactivity were encountered. Immediately after removal, the reaction was quenched by the addition of 1.00 ml. of 0.3*N* di-*n*-butylamine in 10 ml. of toluene to 4.95 ml. of reaction mixture, heating to a boil, and diluting with 20 ml. of methanol. Analysis for the residual isocyanate present in each sample was then accomplished by titrating the excess di-*n*-butylamine remaining after reaction, with 0.0100*N* hydrochloric acid to the endpoint indicated by bromphenol blue indicator.

Infrared Absorption Spectra as Evidence for Complexation

In an effort to obtain an independent confirmation of complexation by metal salts, infrared spectra were obtained first of the polyol, isocyanate, and catalyst separately in toluene. Next, spectra for combinations of each of the first two reagents with the catalyst were taken. Finally, all three reagents together were observed. Comparisons of the various infrared spectra were made in order to detect any shifts in absorption due to complexation. All spectra were taken in a Perkin-Elmer Infracord using 0.105 mm. cell with toluene compensation.

Results of Kinetic Work

The results of this investigation are presented in Tables I–III. Table I depicts the effects of catalyst and functional group on specific rate. The effect of polyfunctionality in the alcohol function is shown in Table II. Finally, Table III gives the data for the effect of a polyfunctional isocyanate.

TABLE I
Catalysis of the Reaction of the Monofunctional Reagents

Active hydrogen compounds	Temp., °C.	Specific rate constants (one per mole hour) Triethylenediamine	Stannous 2-ethylhexoate	Cobaltous stearate	Sodium salt of M-II
1-Butanol	35.5	14.0 ± 0.2			
2-Butanol	35.5	2.28 ± 0.02			
M-I[a]	35.5	1.14 ± 0.01			
M-II[b]	35.5	1.10 ± 0.01	2.28 ± 0.08	3.23 ± 0.08	0.278 ± 0.005
Butyl-*N*-phenyl carbamate	35.5	0.114 ± 0.002 (initial)			
Ethyl-*N*-ethyl carbamate	35.5	0.108 ± 0.002 (initial)	0.081 ± 0.014 (initial)		

[a] 2-Hydroxybutyl butyl ether.
[b] 1-Ethyl-1-(2-hydroxybutyl)-2-butoxyethane.

TABLE II
Catalysis of the Reaction of Polyfunctional Alcohols with Phenyl Isocyanate

Alcohol	Temp., °C.	Specific rate constant (one per mole hour) Triethylenediamine	Stannous 2-ethylhexoate	Cobaltous stearate
P-I	35.5	2.54 ± 0.08	17.64 ± 0.24	5.04 ± 0.18
P-II	35.5	13.4 ± 0.2	23.1 ± 0.6	5.26 ± 0.10
P-III	35.5		27.9 ± 0.5	

TABLE III
Catalysis of the Reaction of Polyfunctional Alcohols with Tolylene Diisocyanate

Alcohol	Temp., °C.	Specific rate constants (1/mole hr.) Triethylenediamine	Stannous 2-ethylhexoate
P-I	35.5		9.12 ± 0.12
P-II	35.5	8.61 ± 0.03	15.2 ± 0.3
P-II + 25% tetramethyl butanediamine	35.5		32.2 ± 0.2
P-III	35.5		105.0 ± 0.5

Interpretation of Results

Several facts become very apparent from the data. First, the type of functional group present in the active hydrogen compound has a decided effect (Table I) on the reaction rate. Thus, a primary hydroxyl group reacts six times as fast as a secondary under triethylenediamine catalysis. If a beta ethereal group is present, as in M-I, the specific rate is half that for the compound with no ethereal group, e.g., 2-butanol. However, additional ethereal groups, as in M-II, have essentially no effect. The retarding effect of beta ethers is probably an electron withdrawing effect which reduces the nucleophilicity of the hydroxyl group and thus its reactivity. If the hydrogen donor is a urethane group, the specific rate is only one-twentieth that for secondary alcohols, and the reaction, unlike those for the alcohols, equilibrates at 25% completion.

Since the monohydroxyl polyether, M-II, mentioned above has structural similarities to the polyhydroxy polyethers also investigated, the former compound was used to study the effect of the different catalysts on the monofunctional system. As Table I shows, the relative catalytic activity appears to be cobaltous stearate > stannous 2-ethylhexoate > triethylenediamine > sodium salt of M-II. In the reaction of ethyl-N-ethylcar-

bamate, however, it is interesting to observe that for the catalysts studied this activity series is reversed. Since the only difference in the two cases was the hydrogen donor, it appears to indicate that the stannous salt unlike the tertiary amine must complex to this species or to both reactants, otherwise there should be little or no difference in the relative activities observed.

To further elucidate the mode of catalysis by the metal salts, a study was made on the reaction of the polyhydroxy polyethers with phenyl isocyanate, and the results are presented in Table II. All three catalysts imparted higher rates of reaction to the secondary hydroxyl groups in the polyhydroxy polyether, P-I, as compared to the secondary hydroxyl group in the monohydroxy diether, M-II. However, the enhancements were not all identical. The tertiary amine and cobaltous stearate produced only twofold enhancements while the stannous salt resulted in a ninefold increase. Since it has been postulated that triethylenediamine acts by activation of only one reactant, the isocyanate,[1-4] it might seem plausible that the cobalt also activates only one.

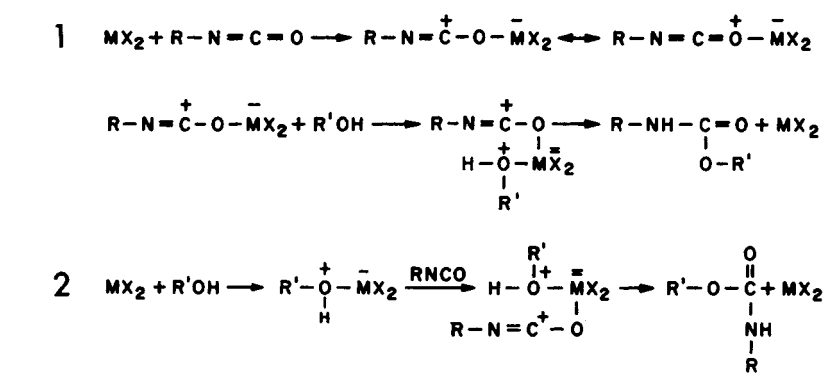

Fig. 2. Mechanism of metal salt catalysis.

The stannous salt based on its much greater activity, appears to activate both reagents. This activation could be accomplished by the formation of a ternary complex of the reactants and the catalyst (Fig. 2). In this complex, several hydroxyl groups, both complexed and not, would be held within attacking distance of the isocyanate group. Thus, the effective hydroxyl group concentration about the isocyanate would be greater than the solution concentration, and hence result in the rate enhancement observed.

When the polyhydroxy polyether containing 50% primary hydroxyls, P-II, was investigated, it was noted that while the amine catalyst showed a sixfold increase in reaction rate over the reaction with P-I, the metal salts showed only a slight or no enhancement. The acceleration observed with the amine is the same as that exhibited for the monofunctional alcohols. This effect would be the result predicted by Baker's mechanism,[1,2] because in both cases the same isocyanates are being activated and the

differences in steric requirements of the secondary versus primary alcohols would be the same for the mono- and polyfunctional cases.

The results for tin catalysis fit in nicely with the proposed mode of catalysis (Fig. 2). In a three-membered complex, as postulated, the steric requirements of the hydroxyls would have only a minor effect, namely, that due to a slight modification of the complex structure due to steric hindrance.

The data for cobalt catalysis were especially interesting. As was previously pointed out, it might appear that cobalt activates only one reactant. If so, then that reactant must be the alcohol, because activation of the alcohol is the only way that a twofold rate enhancement for polyols over monohydroxy alcohols can be correlated with no enhancement for primary over secondary hydroxyls in polyols. However, it seems that if the cobalt salt did indeed activate only the alcohol, then primary hydroxyls should react faster due to less hindrance to isocyanate attack. The fact that this is not the case argues for a ternary complex similar to that for tin, Figure 3.

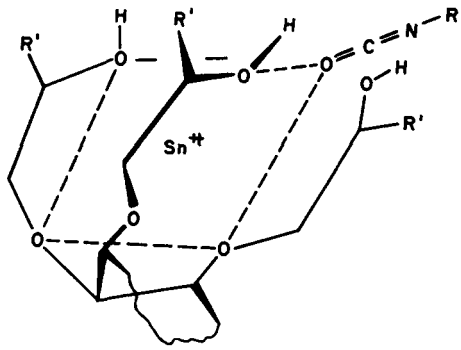

Fig. 3. Stannous complex.

Since complexation, as shown by the infrared studies and by increased solubility of the salts in the solvents used, is very rapid, the rate determining step must be the reaction between the ligands after complexation. Therefore, the differences in the activity of the stannous and cobaltous salts probably lies in the structure of the complexes formed. The available data suggest that both the stannous ion and the cobaltous ion coordinate to four ligand groups, the former in the square planar configuration (Fig. 2) and the latter in the tetrahedral configuration (Fig. 3).[9] In addition, the square planar structure is more favorable to complexation to compounds such as the β-hydroxy ethers studied here than is the tetrahedral.[9] It should be noted that the kinetics allow only one hydroxyl compound and one isocyanate compound in the transition state of the rate determining step.[10] Thus, although several hydroxyl groups, all contained in one molecule, are shown in Figures 2 and 3 only one isocyanate group may be present because this compound is monofunctional. Because this last restriction is the same for both catalysts, the activity difference must be due to less favorable positioning of the hydroxyl groups for interaction with the

isocyanate in the cobalt complex versus that in the tin complex. This difference might be the result of the fact that the hydroxyl groups complexed to cobalt unlike those complexed to tin cannot lie in the same plane as the isocyanate group. Thus, any overlap of bond orbitals would be diminished. In addition, the distance between the hydroxyl groups and the isocyanate group might be greater in the cobalt complex than in the tin due to less favorable complexation of the β-hydroxy ethers in the former.

If an effort to determine if a combination of the two types of catalyst investigated, tertiary amines and metal salts would be synergistic; an amine-based polyol, P-III, was allowed to react with phenyl isocyanate under catalysis with stannous 2-ethylhexoate. The specific reaction rate (Table II) of P-III was indeed faster than for the comparable polyol P-II. Since the activity of tertiary amines depends a great deal on the steric requirements of the amine and since the amino groups of polyol P-III have very large steric requirements, the observed enhancement does indicate a synergistic and not an additive catalytic effect.

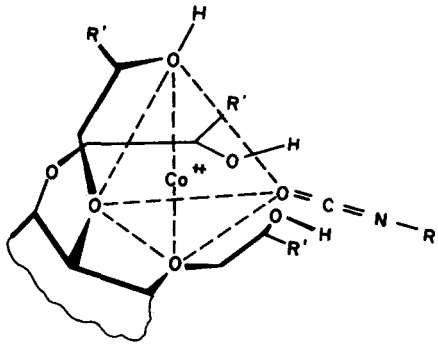

Fig. 4. Cobaltous complex.

To complete the study, it was desired to determine the effect of polyfunctionality in the isocyanate. For this purpose, the commercially available tolylene diisocyanate was employed in reactions with the three polyols just considered. It was very evident from the data for polyols P-I and P-II that only one of the isocyanates was reacting at a time. This result would follow naturally from the observations made in the literature that due to steric hindrance an *ortho*-isocyanate group in tolylene diisocyanate is ten times less reactive than a *para*-group.[11,12] The stepwise reaction of the isocyanate groups then would cut the effective isocyanate concentrations in half producing the results observed. The fact that the rates for polyol P-II were not quite half with tolylene diisocyanate as compared to phenyl isocyanate was probably due to the presence of tertiary amine in the polyol.

A very surprising result was obtained with P-III. Instead of a reduction in specific rate a fourfold enhancement over that for phenyl isocyanate was observed. Because this polyol was based on an amine, a synergistic effect

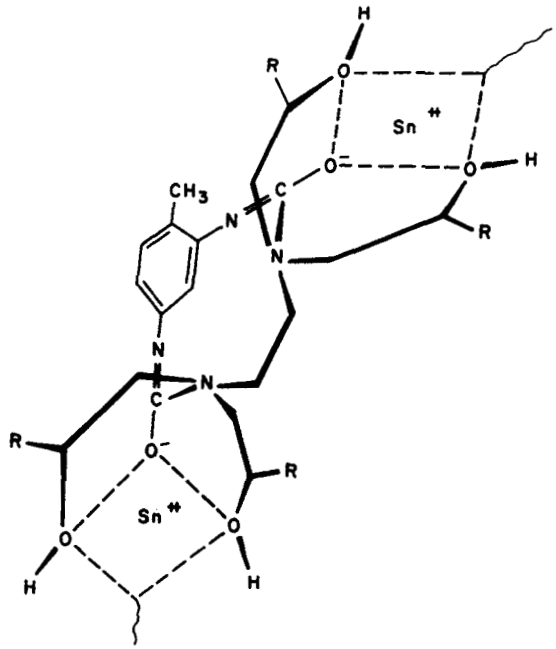

Fig. 5. Polyol P-III and tolylene diisocyanate under tin catalysis.

was suspected as the cause of this rate increase. However, when polyol P-II and an amount of tetramethyl butanediamine equivalent to the amino groups in polyol P-III were substituted for the latter polyol, only a small rate enhancement was observed over the reaction of P-II with phenyl isocyanate under tin catalysis. Since synergism is not the principal cause of the rate enhancement, it must be the polyol structure. This effect is such

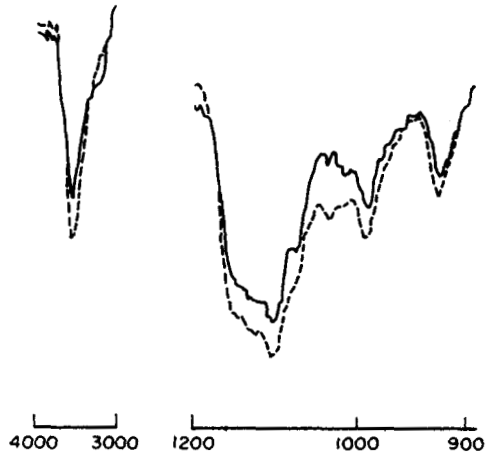

Fig. 6. Infrared of the polyol with and without catalyst: (- - -) polyol and (—) polyol plus catalyst.

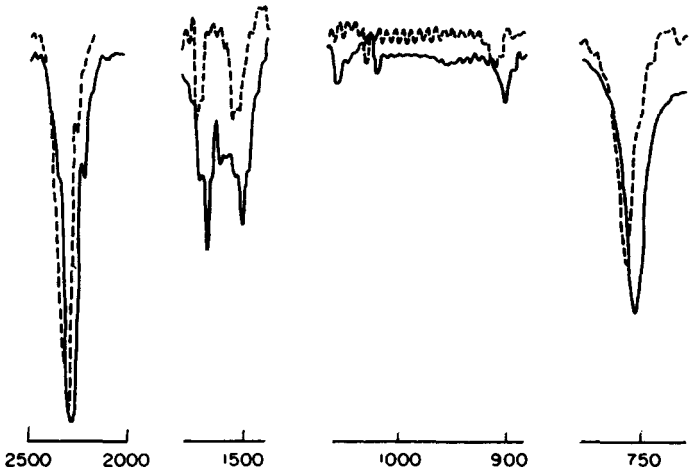

Fig. 7. Infrared of the isocyanate with and without catalyst: (- - -) isocyanate and (—) isocyanate plus catalyst.

that the two amino groups could activate both isocyanate groups simultaneously and in addition to the tin catalysis (Fig. 4).

Infrared Investigation

To obtain confirmation of the presence of the postulated ternary complex for tin catalysis, comparisons were made of the spectra of the polyol (P-I), phenyl isocyanate, and stannous 2-ethylhexoate with mixtures of each reactant and the catalyst and then all three reagents. Figure 5 shows the results for poly P-III and tolylene diisocyanate under tin catalysis. Figure 6 shows the results for the polyol and catalyst, and Figure 7 for the isocyanate.

The polyol showed shifts at 3460, 1030, and 990 cm.$^{-1}$ for the hydroxyl

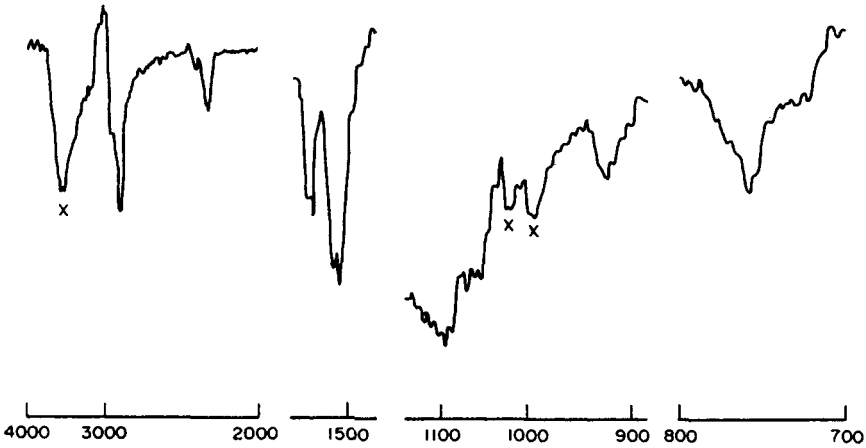

Fig. 8. Infrared spectrum of all three reagents: (X) twin hydroxyl peaks.

groups as well as shifts at 1080 and 1055 cm.$^{-1}$ for the ethereal groups. The isocyanate compound showed shifts at 2270, 1605, 1075, 1030, and 910 cm.$^{-1}$ for the isocyanate group while other shifts for the monosubstituted phenyl group occurred at 1500 and 757 cm.$^{-1}$. Thus, the catalyst appears capable of complexation with either reagent alone.

When all three reagents were mixed and the peaks for the reaction product were eliminated, the same shifts noted above were observed (Fig. 8). It was of interest to note that the hydroxyl group absorptions showed split peaks, one characteristic of the complexed hydroxyl group and one for the uncomplexed, at 3460, 1030, and 990 cm.$^{-1}$. All the isocyanate and ethereal groups remained complexed. This result indicated that some of the hydroxyl groups had been displaced from the complex by introduction of the isocyanate group and thus gives a very good indication of the presence of the ternary complexes postulated.

The evidence obtained in this study indicates that the metal salts, unlike tertiary amines, may catalyze by activation of both reactants by means of a ternary complex. In addition, the activity of the metal salts depends on their ability to form a complex in which the two reacting groups are held in their optimum position for reaction. This property in turn depends on the coordination number of the metal ion, the configuration of the complex, and the ionic radius of the ion.

References

1. Baker, J. W., and J. B. Holdsworth, *J. Chem. Soc.*, **1947**, 713.
2. Baker, J. W., J. Gaunt, and M. M. Davies, *J. Chem. Soc.*, **1949**, 9.
3. Tazema, J. J., and H. K. Latourette, paper No. 35, presented at the 130th meeting of the American Chemical Society, Division of Paint, Plastics, and Printing Ink Chemistry, Atlantic City, N. J., Sept. 1956.
4. Farkas, A., and K. G. Flynn, *J. Am. Chem. Soc.*, **82**, 642 (1950).
5. Britain, J. W., and P. G. Gemeinhardt, *J. Appl. Polymer Sci.*, **4**, 207 (1960).
6. Tarbell, D. S., R. C. Mallatt, and J. W. Wilson, *J. Am. Chem. Soc.*, **64**, 2229 (1942).
7. Bailey, M. E., C. E. McGinn, and R. G. Spaunbergh, paper No. 36, presented at the 130th meeting of the American Chemical Society, Division of Paint, Plastics, and Printing Ink Chemistry, Atlantic City, N. J., Sept. 1956.
8. Mack, G. P., *Chem. Processing*, **1960**, p. 33.
9. Bailar, J. C., Jr., *The Chemistry of the Coordination Compounds*, Reinhold, New York, 1956, pp. 374, 375, and 240-1.
10. Weisfeld, L. B., *J. Chem. Educ.*, **38**, 88 (1961).
11. Morton, M., and M. A. Deisz, paper No. 34, presented at the 130th meeting of the American Chemical Society, Division of Paint, Plastics, and Printing Ink Chemistry, Atlantic City, N. J., Sept. 1956.
12. McGinn, C. E., and R. G. Spaunbergh, paper No. 38, presented at the 130th meeting of the American Chemical Society, Division of Paint, Plastics, and Printing Ink Chemistry, Atlantic City, N. J., Sept. 1956.

Synopsis

In an effort to further elucidate the mode of catalysis of metal salts in the urethane reaction, monofunctional compounds of various types and polyfunctional alcohols were allowed to react with either phenyl isocyanate or tolylene diisocyanate (80/20 mixture

of 2,4- and 2,6-isomers) under catalysis by a tertiary amine or one of two metal salts. With the monofunctional compounds, the relative activity of the catalysts was cobaltous stearate > stannous 2-ethylhexoate > triethylenediamine. With polyfunctional compounds, however, the positions of the salts in this activity series are reversed. Evidence is presented based upon reaction kinetics and infrared spectra for the presence of a ternary complex as the reactive intermediate in the reaction catalyzed by metal salts. It is postulated that the high activity of some metal salts, such as stannous 2-ethylhexoate, can be attributed to the formation of a ternary complex which holds the functional groups in the optimum positions for reaction. Less optimum positions resulting from a different geometry of the coordination complex, lead to lower activity as observed with cobaltous stearate.

Résumé

Dans le but d'élucider d'avantage le mode de catalyse des sels métalliques dans les réactions de l'uréthanes, on a fait réagir des composés monofonctionnels de différents types et des alcools polyfonctionnels avec l'isocyanate de phényle ou le diisocyanate de tolylène (mélange 80/20 des isomères 2,4 et 2,6) avec une amine tertiaire ou un des deux sels métalliques comme catalyseur. Avec les composés monofonctionnels, les activités relatives des catalyseurs sont: stéarate de cobalt > 2 éthylhexoate d'étain > triéthylène diamine. Cependant, avec les composés polyfonctionnels la position des sels est inversée dans cette série d'activité. Sur la base de la cinétique de la réaction et des spectres infra-rouges, on démontre la présence d'un complexe ternaire comme intermédiaire réactionnel dans la réaction catalysée par des sels métalliques. On postule que l'activité d'étain, peut être attribuée à la formation de complexes ternaires qui maintiennent les groupes fonctionnels dans la position optimale pour la réaction. Les positions moins favorisées, résultant d'une géométrie différente du complexe de coordination, conduisent à une activité plus faible comme on a pu l'observer pour le stéarate de cobalt.

Zusammenfassung

Um die Katalysatorwirkung von Metallsalzen bei der Urethanreaktion weiter aufzuklären, wurden monofunktionelle Verbindungen verschiedener Art und polyfunktionelle Alkohole entweder mit Phenylisocyanat oder mit Toluylenisocyanat (80/20-Mischung der 2,4- und 2,6-Isomeren) unter Katalyse durch ein tertiäres Amin oder durch eines von zwei Metallsalzen zur Reaktion gebracht. Bei den monofunktionellen Verbindungen lag die relative Aktivität der Katalysatoren in der Reihe Kobaltstearat > Zinn-2-Äthylhexoat > Triäthylendiamin. Bei polyfunktionellen Verbindungen wird jedoch die Stellung der Salze in dieser Aktivitätsreihe umgekehrt. Auf Grund der Reaktionskinetik und Infrarotspektren wird bei der Katalyse mit Metallsalzen das Vorhandensein eines ternären Komplexes als reaktionsfähiges Zwischenprodukt bei der Reaktion angenommen. Die hohe Aktivität einiger Metallsalze, wie Zinn-2-äthylhexoat, wird der Bildung eines ternären Komplexes zugeschrieben, der die funktionellen Gruppen in der für die Reaktion optimalen Lage hält. Weniger günstige Anordnungen, die durch eine verschiedenartige geometrische Anordnung des Koordinationskomplexes bedingt sind, führen zu einer geringeren Aktivität, wie sie bei Kobaltstearat beobachtet wird.

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