Structural Effects in Metal Ion Catalysis of Isocyanate–Hydroxyl Reactions

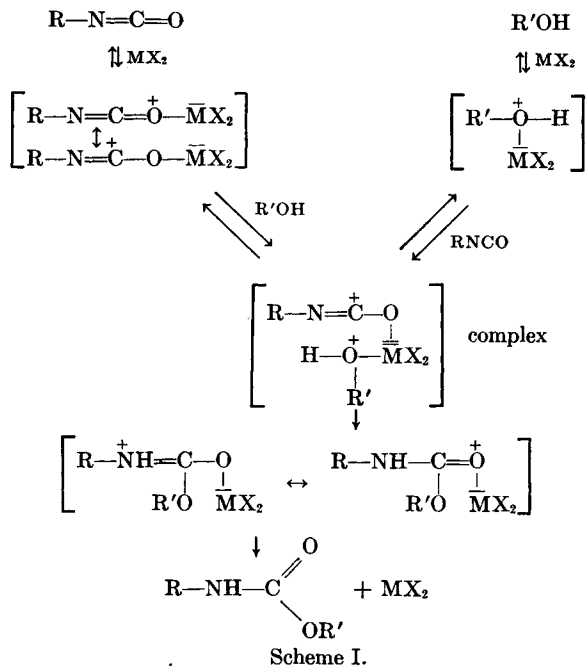JANIS ROBINS, *Minnesota Mining & Manufacturing Company,*
St. Paul, Minnesota

Synopsis

Metal ion catalysis of isocyanate–hydroxyl reactions is considerably enhanced by the presence of certain "activating" groups α, β, even γ to the carbon carrying the reactive hydroxyl. Few metal ions can significantly catalyze the isocyanate–butanol reaction. In general the metal ion catalysts fall into two groups: catalysts which maintain a fair portion of their activity, even in systems containing hindered isocyanates, and catalysts which are very sensitive to changes in steric factors. It is believed that metal ions fulfill a twofold function: they increase the electrophilic character of the isocyanate group by coordinating either at the oxygen or nitrogen, and they bring the isocyanate and alcohol in closer proximity. The "activating" groups are believed to have two major opposing effects: to increase the overall stability of the ternary complex while allowing the hydroxyl group to retain most of its nucleophilicity and to produce in some cases urethanes which preferentially chelate the metal ion and kill the catalysis. All metal ions exhibit greater catalytic activity in systems containing 1,2- than 1,4-glycols; furthermore the sensitivity to steric hindrance increases from 1,2- to 1,4-glycols, indicating that only chelation can sufficiently increase the stability of the ternary complex to produce the maximum catalytic effect.

INTRODUCTION

Recently Britain and Gemeinhardt[1] and Smith[2] have suggested a mechanism for metal compound catalysis of isocyanate–hydroxyl reactions involving the formation of a ternary complex (scheme I).

Britain and Gemeinhardt found that the metal compound catalysts fell into two major groups. Group 1 included stannous, lead, bismuth, and organotin compounds which activated aliphatic diisocyanates more than tolylene diisocyanate so that the relative rates of the diisocyanate reactions were approximately equal. Group 2 included zinc, cobalt, iron, stannic, antimony, and titanium compounds which had a much larger effect on the aliphatic diisocyanates, so that these isocyanates were faster to react with hydroxyl groups than tolylene diisocyanate. They suggested that this is due to steric factors (the aliphatic diisocyanates used were sterically unhindered, whereas the 2 and 6 positions on the tolylene diisocyanate were hindered by the methyl group in the 1 position). They further suggested that if the metal compound did not have the ability to complex with the incoming hydroxyl compound and the isocyanate group in such a way that the hydroxyl group and the isocyanate nitrogen are brought close together,

$$R—N{=}C{=}O \qquad\qquad R'OH$$

$$\updownarrow MX_2 \qquad\qquad\qquad \updownarrow MX_2$$

$$\left[\begin{array}{c} R—N{=}C{\overset{+}{=}}\bar{O}—MX_2 \\ \updownarrow + \\ R—N{\overset{+}{=}}C—O—\bar{M}X_2 \end{array}\right] \qquad \left[\begin{array}{c} R'—\overset{+}{O}—H \\ | \\ \bar{M}X_2 \end{array}\right]$$

$$\left[\begin{array}{c} R—N{\overset{+}{=}}C—O \\ | \\ H—\overset{+}{O}—\bar{\bar{M}}X_2 \\ | \\ R' \end{array}\right] \text{complex}$$

$$\downarrow$$

$$\left[\begin{array}{cc} R—\overset{+}{N}H{=}C—O & R—NH—C{\overset{+}{=}}O \\ \quad| \quad | & \quad | \quad | \\ R'\bar{O} \quad \bar{M}X_2 & \leftrightarrow \quad R'\bar{O} \quad \bar{M}X_2 \end{array}\right]$$

$$\downarrow$$

$$R—NH—C\overset{\displaystyle O}{\underset{\displaystyle OR'}{\diagup\!\!\!\diagdown}} \quad + MX_2$$

Scheme I.

the catalytic activity would be due only to the acidity or basicity of the compound.

Smith[2] has criticized this mechanism and has pointed out that it requires an attack of one electron deficient center on another and therefore would be unlikely. He proposed an alternate mechanism in which the alcohol complexes with the metal ion at some site other than the reactive hydroxyl.

Since he found that several polyether polyols in presence of stannous 2-ethyl hexoate or cobaltous stearate reacted with phenyl isocyanate considerably faster than 1-ethyl-1-(2-hydroxybutyl)-2-butoxyethane, he concluded that polyfunctionality is necessary to bring out the full catalytic activity of cobaltous but especially stannous ion. Recently Fischer[3] has presented evidence for neighboring group effects in metal ion catalysis of nitro diisocyanates with nitro diols. Only metal chelate (acetyl acetonates) catalysts, however, were investigated.

The present investigation was conducted in an effort to screen a large number of metal compounds in a variety of isocyanate–hydroxyl reaction systems. A number of very interesting observations have been made pertaining to the mechanism of metal ion catalysis of isocyanate–hydroxyl reactions.

EXPERIMENTAL

Materials

Dioxane, spectro grade (Matheson, Coleman and Bell) was used as solvent for all heat-rise experiments. The following isocyanates were used: phenyl isocyanate, o-tolyl isocyanate, o-methoxyphenyl isocyanate, (all

reagent grade) Allied Chemical Corporation; TDI prepolymer (91% 80/20 toluene diisocyanate, 9% trimethylol propane, heated to 150°C.).

The following hydroxy compounds were used: 1-butanol (redistilled), ethylene glycol, 2-ethoxyethanol, β-dimethylaminoethanol, 1-4-butylene glycol, (all reagent grade), neopentyl glycol (recrystallized), ethylene glycol, monoacetate (redistilled), all Eastman Kodak; ethylthioethanol (practical), Pennsalt. As catalysts the following metal compounds were used: chromium naphthenate (Cr^{+3}), manganese octoate (6% Mn^{+2}), zinc naphthenate (8% Zn^{+2}), nickel naphthenate (6% Ni^{+2}), cadmium naphthenate (Cd^{+2}), all from Advance Solvents and Chemicals; iron octoate (6% Fe^{+3}), cobalt octoate (6% Co^{+2}), indium naphthenate (6% In^{+3}), antimony octoate (Sb^{+3}), lead octoate (24% Pb^{+2}), mercuric naphthenate (24% Hg^{+2}), bismuth naphthenate (12% Bi^{+3}), all from Nuodex Products Company; copper octoate (8% Cu^{+2}), Harshaw Chemical Company; dibutyltin dilaurate (Bu_2Sn^{+2}), stannous octoate (Sn^{+2}), Metal & Thermit Corporation.

Procedure

In order to screen effectively a large number of metal compounds in a variety of reaction mixtures it was necessary to devise a rapid testing method. As the isocyanate–alcohol reaction is rather exothermic it was decided to follow the reaction rate calorimetrically by measuring heat rise versus time for $1M$ isocyanate–alcohol solutions in dioxane containing almost 2% catalyst. All the reactions were started at room temperature (25–27°C.), and the heat rise of about 35 ± 1°C. represented complete reaction (as indicated by infrared spectra of the resulting solutions).

An insulated and covered polyethylene-lined paper cup served as the reaction vessel. Stirring was achieved by a magnetic stirrer, and the temperature was recorded by use of a thermocouple. As most of the effective reactions were completed in 5 min., only a small amount of heat was lost to the surroundings. It is obvious that small differences in reactivity or catalytic activity could not be detected in this manner but this method was designed to show up especially large differences. It is believed that the subsequent results will produce sufficient justification for this approach.

RESULTS

This investigation comprises a large variety of alcohols, isocyanates, and metal-ion catalysis. Results are shown in Tables I–XII and Figures 1–7.

The metal ion catalysts for the 1-butanol–isocyanate system (Table I) fell more or less into two groups: (1) metal ions which were fairly good catalysts (e.g., Fe^{+3}, Mn^{+2}, Bi^{+3}, Bu_2Sn^{+2}); (2) metal ions which exhibited a rather low catalytic activity (e.g., Hg^{+2}, Cu^{+2}). All the catalysts (with the exception of probably Bu_2Sn^{+2}) lost most of their catalytic activity in systems containing sterically hindered isocyanates.

In the ethylene glycol–isocyanate system (Table II), it is interesting to note the extreme catalytic activity for most metal ions, especially the ones which showed poor activity in the 1-butanol–isocyanate system. The

TABLE I
Catalyzed 1-Butanol–Isocyanate Reaction

| | 1-min. heat rise, °C. | | | |
Catalyst	Phenyl isocyanate	o-Tolyl isocyanate	o-Methoxy-phenyl isocyanate	TDI prepolymer
Chromium(III) naphthenate	0			
Manganese(II) octoate	18	1	0	4
Iron(III) octoate	5	2		4
Cobalt(II) octoate	3	<1		2
Nickel(II) naphthenate	2			
Copper(II) octoate	1	1		1
Zinc(II) naphthenate	1	1		1
Cadmium(II) naphthenate	2			
Indium(III) naphthenate	1			
Tin(II) octoate	4	1		2
Antimony(III) octoate	5	1		2
Mercury(II) naphthenate	3	1		2
Lead(II) octoate	4	1	1	2
Bismuth(III) naphthenate	18	1	4	8
Dibutyltin(IV) dilaurate	35	3	15	14
None	0	0	0	0

metal ions could be segregated into three groups: (1) catalysts which maintained fair catalytic activity even in face of considerable steric hindrance at the isocyanate group (e.g., Pb^{+2}, Bi^{+3}, Bu_2Sn^{+2}); (2) catalysts which were very sensitive to steric factors (e.g., Mn^{+2}, Co^{+2}, Zn^{+2}); (3) catalysts

TABLE II
Catalyzed Ethylene Glycol–Isocyanate Reaction

| | 1-min. heat rise, °C. | | | | |
Catalyst	Phenyl isocyanate	o-Tolyl isocyanate	Durene diiso-cyanate	TDI pre-polymer	Phenyl thioiso-cyanate
Chromium(III) naphthenate	2			1	
Manganese(II) octoate	34	2	1	10	0
Iron(III) octoate	33	32	1	6	
Cobalt(II) octoate	35	5	1		
Nickel(II) naphthenate	15			13	
Copper(II) octoate	5	1		6	
Zinc(II) naphthenate	21	3		4	
Cadmium(II) naphthenate	35			10	
Indium(III) naphthenate				13	
Tin(II) octoate	35	32	4	31	
Antimony(III) octoate	35	21	5	31	0
Mercury(II) naphthenate	35	11	2	21	0
Lead(II) octoate	35	32	17	34	0
Bismuth(III) naphthenate	35	19	8	31	0
Dibutyltin(IV) dilaurate	35	26	4	34	0
None			0		0

TABLE III
Catalyzed 2-Ethoxyethanol–Isocyanate Reaction

Catalyst	1-min. heat rise, °C.			
	Phenyl isocyanate	o-Tolyl isocyanate	o-Methoxy-phenyl isocyanate	TDI prepolymer
Chromium(III) naphthenate				
Manganese(II) octoate	1	0	0	2
Iron(III) octoate	4	2	0	2
Cobalt(II) octoate	7			8
Nickel(II) naphthenate				
Copper(II) octoate				
Zinc(II) naphthenate	1			
Cadmium(II) naphthenate	2			8
Indium(III) naphthenate	20	1		
Tin(II) octoate	30	2	3	20
Antimony(III) octoate	20	1		25
Mercury(II) naphthenate	20	5	2	18
Lead(II) octoate	30	6	16	23
Bismuth(III) naphthenate	7	1		15
Dibutyltin(IV) dilaurate	34	3	11	19
None			0	

which in general were rather poor in promoting the above reaction (e.g., Cr^{+3}, Cu^{+2}, In^{+3}).

No catalytic activity was observed in systems containing phenyl thio-isocyanate.

TABLE IV
Catalyzed Ethyl Thioethanol–Isocyanate Reaction

Catalyst	1-min. heat rise, °C.		
	Phenyl isocyanate	o-Tolyl isocyanate	TDI prepolymer
Chromium(III) naphthenate			
Manganese(II) octoate	1	0	2
Iron(III) octoate	5	3	3
Cobalt(II) octoate	21	1	9
Nickel(II) naphthenate			
Copper(II) octoate	7	1	3
Zinc(II) naphthenate	1	0	
Cadmium(II) naphthenate	7	1	14
Indium(III) naphthenate	4	0	2
Tin(II) octoate	33	5	24
Antimony(III) octoate	7	1	24
Mercury(II) naphthenate	33	14	29
Lead(II) octoate	33	9	28
Bismuth(III) naphthenate	7	1	16
Dibutyltin(IV) dilaurate	38	6	24
None	0	0	0

TABLE V
Catalyzed β-Dimethylaminoethanol–Isocyanate Reaction

Catalyst	1-min. heat rise, °C.					
	Phenyl iso-cyanate	o-Tolyl iso-cyanate	o-Meth-oxy-phenyl iso-cyanate	Durene diiso-cyanate	TDI pre-polymer	Phenyl thioiso-cyanate
Chromium(III) naphthenate					17	
Manganese(II) octoate			3		20	
Iron(III) octoate					20	<1
Cobalt(II) octoate			3		24	
Nickel(II) naphthenate					19	
Copper(II) octoate	33	33		32	35	7
Zinc(II) naphthenate						
Cadmium(II) naphthenate					21	
Indium(III) naphthenate					31	
Tin(II) octoate			31			
Antimony(III) octoate			6		26	
Mercury(II) naphthenate			21		33	
Lead(II) octoate			33		35	
Bismuth(III) naphthenate			33		35	
Dibutyltin(IV) dilaurate					26	
None	29	12	3	18	17	0

Some catalysts (Mn^{+2}, Fe^{+2}, Co^{+2}, Zn^{+2}, Cd^{+2}, Bi^{+3}) showed considerable deactivation (even with phenyl isocyanate) in the 2-ethoxyethanol–isocyanate system (Table III), compared to the ethylene glycol–phenyl isocyanate system. Furthermore, the effect of o-methyl group on the reac-

TABLE VI
Catalyzed 2-Hydroxyethyl Acetate–Isocyanate Reaction

Catalyst	1-min. heat rise, °C.		
	Phenyl isocyanate	o-Tolyl isocyanate	TDI prepolymer
Chromium(III) naphthenate			
Manganese(II) octoate	9	2	
Iron(III) octoate	20	15	16
Cobalt(II) octoate	16	2	13
Nickel(II) naphthenate	6		
Copper(II) octoate	2		
Zinc(II) naphthenate	6		
Cadmium(II) naphthenate	6		
Indium(III) naphthenate	22	1	
Tin(II) octoate	22	9	16
Antimony(III) octoate	24	4	16
Mercury(II) naphthenate	18	6	10
Lead(II) octoate	32	19	22
Bismuth(III) naphthenate	24	6	16
Dibutyltin(IV) dilaurate	39	7	21
None			0

TABLE VII
Catalyzed Neopentyl Glycol–Isocyanate Reaction

	1-min. heat rise, °C.			
Catalyst	Phenyl isocyanate	o-Tolyl isocyanate	Durene diisocyanate	TDI prepolymer
Chromium(III) naphthenate				
Manganese(II) octoate	3	0		1
Iron(III) octoate	40	30		7
Cobalt(II) octoate	1	0		8
Nickel(II) naphthenate	27	1		
Copper(II) octoate	11	0		
Zinc(II) naphthenate	3	0		
Cadmium(II) naphthenate	1	0		
Indium(III) naphthenate	1	0		
Tin(II) octoate	40	12		22
Antimony(II) octoate	30	2	7	31
Mercury(II) naphthenate	12	2		5
Lead(II) octoate	39	6		14
Bismuth(III) naphthenate	10	5		14
Dibutyltin(IV) dilaurate	38	4		15
None				0

tivity of the phenyl isocyanate was most significant: almost all catalysts were severely deactivated.

In most respects the ethyl thioethanol–isocyanate system (Table IV) was very similar to the 2-ethoxyethanol–isocyanate system. A few cata-

TABLE VIII
Catalyzed 1,4-Butylene Glycol–Isocyanate Reaction

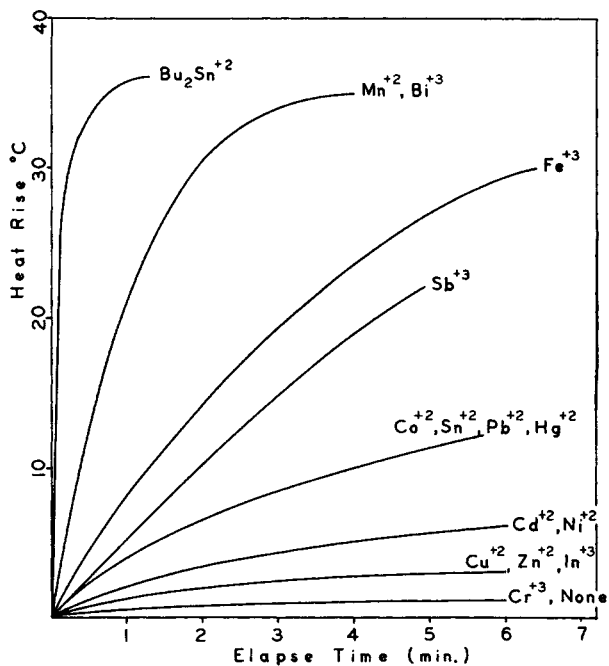|	1-min. heat rise, °C		
Catalyst	Phenyl isocyanate	o-Tolyl isocyanate	TDI prepolymer
Chromium(III) naphthenate			
Manganese(II) octoate	1		1
Iron(III) octoate	5	3	3
Cobalt(II) octoate	1		
Nickel(II) naphthenate	1		
Copper(II) octoate	1		
Zinc(II) naphthenate	1		
Cadmium(II) naphthenate	1		
Indium(III) naphthenate	3		
Tin(II) octoate	8	1	
Antimony(III) octoate	9	1	8
Mercury(II) naphthenate	11	2	
Lead(II) octoate	6	2	4
Bismuth(III) naphthenate	7	2	
Dibutyltin(IV) dilaurate	38	7	
None			

Fig. 1. Heat rise vs. time for n-butyl alcohol–phenyl isocyanate system ($1M$ in dioxane).
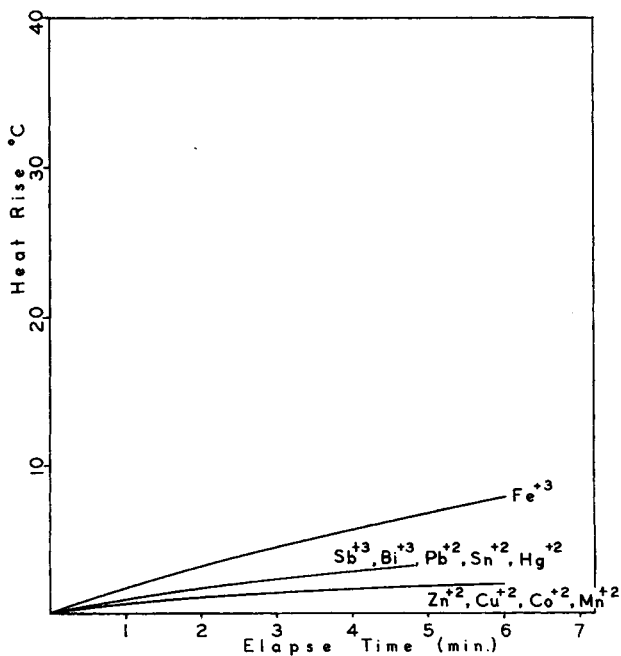

Fig. 2. Heat rise vs. time for n-butyl alcohol–o-tolyl isocyanate system ($1M$ in dioxane).

lysts (Co^{+2}, Hg^{+2}), however, showed particular preference for this system; a few others (Sn^{+2}, Sb^{+3}) seemed to prefer the oxo system.

It is interesting to note the extreme reactivity of the β-dimethylamino-ethyl–isocyanate system (Table V) in absence of any metal-ion catalysts for nonhindered isocyanates. With hindered isocyanates, however, the
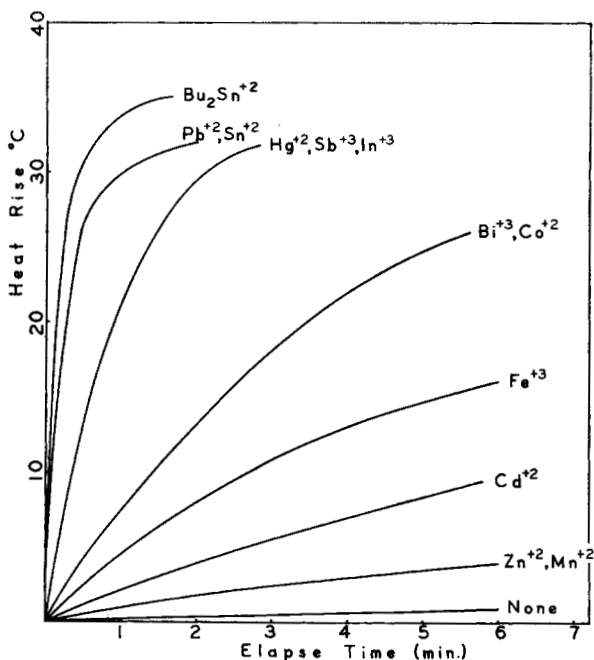

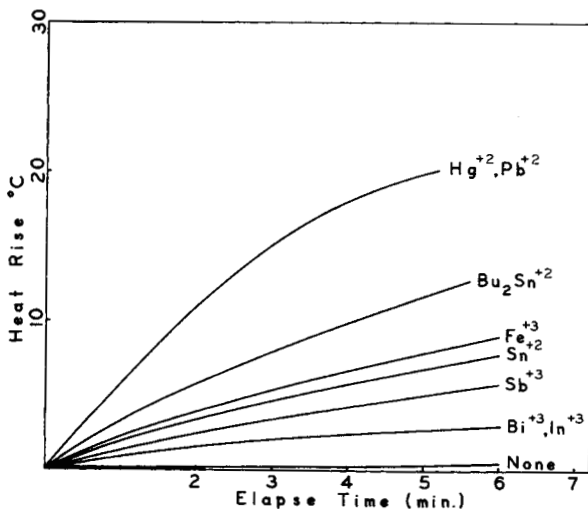Fig. 3. Heat rise vs. time for 2-ethoxyethanol–phenyl isocyanate system (1M in dioxane).

Fig. 4. Heat rise vs. time for 2-ethoxyethanol–o-tolyl isocyanate system (1M in dioxane).

uncatalyzed reaction proceeded rather slowly and appreciable metal ion catalysis was observed.   In this system for the first time significant deacti- vation phenomenon became apparent.   Namely, for some metal ions (Cu^{+2}, Hg^{+2}), a rapid initial reaction was followed by an increasingly slower
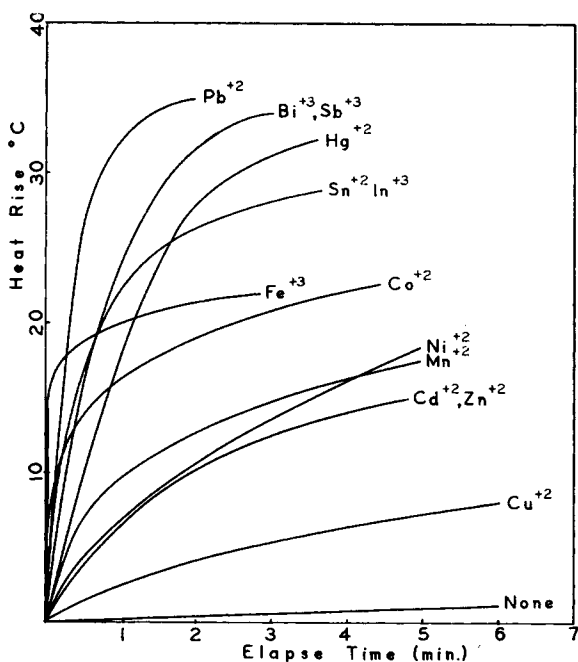
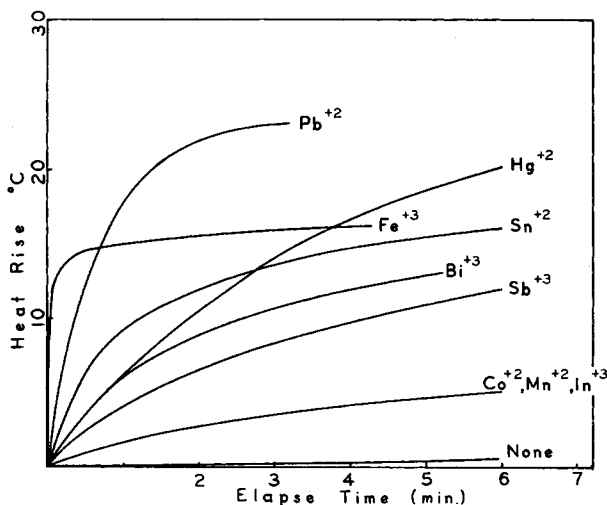Fig. 5. Heat rise vs. time for ethylene glycol monoacetate-phenyl isocyanate system (1M in dioxane).

Fig. 6. Heat rise vs. time for ethylene glycol monoacetate-o-tolyl isocyanate system (1M in dioxane).
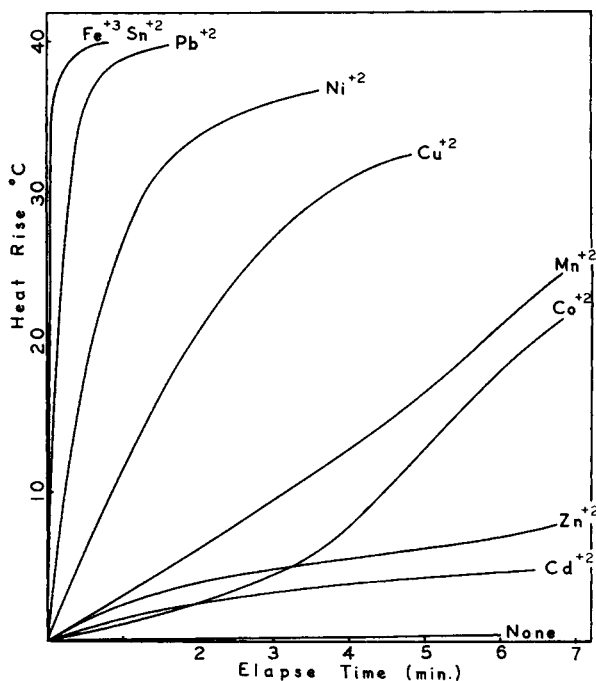
Fig. 7. Heat rise vs. time for neopentyl glycol–phenyl isocyanate system (1M in dioxane).

reaction. In a rudimentary form this behavior seemed to be indicated already for the ethyl thioethanol–isocyanate system (Cd^2).

The phenomenon of latent catalytic deactivation appeared to be exhibited in clear fashion in the 2-hydroxyethyl acetate–isocyanate system (Table VI). Ferric ion served as the most dramatic example, especially in the system containing o-tolyl isocyanate (see Fig. 6). Some evidence for deactivation, however, was shown by most catalysts tested.

A number of metal ions (Ni^{+2}, Cu^{+2}) showed increased activity in the neopentyl glycol–isocyanate system (Table VII) as compared with the system containing ethylene glycol (see Figs. 5 and 7). An interesting catalytic acceleration was observed with Mn^{+2}, Co^{+2}, also Zn^{+2} ions.

It is apparent in the 1,4-butylene glycol–isocyanate system (Table VIII) that the increased separation of the hydroxyl groups produces considerable decrease in the catalytic activity of several metal ions, even in systems containing phenyl isocyanate. However, for a number of catalysts (Sn^{+2}, Sb^{+3}, Hg^{+2}, Pb^{+2}, Bi^{+3}) this system was still considerably more reactive than the simple 1-butanol–isocyanate system. On the other hand, introduction of an o-methyl group in the phenyl isocyanate molecule almost invariably (except for Bu$_2$Sn^{+2}) killed the catalysis.

The 1,5-pentanediol–isocyanate system (Table IX) behaved very much like the previous one (Table VIII). Catalysis was almost eliminated in systems containing o-tolyl isocyanate.

TABLE IX
Catalyzed 1,5-Pentanediol–Isocyanate Reaction

	1-min. heat rise. °C.	
Catalyst	Phenyl isocyanate	o-Tolyl isocyanate
Chromium(III) naphthenate		
Manganese(II) octoate	1	0
Iron(III) octoate	8	3
Cobalt(II) octoate	1	0
Nickel(II) naphthenate	1	0
Copper(II) octoate	1	0
Zinc(II) naphthenate	1	0
Cadmium(II) naphthenate	1	0
Indium(III) naphthenate	1	0
Tin(II) octoate	5	1
Antimony(III) octoate	11	1
Mercury(II) naphthenate	8	2
Lead(II) octoate	6	1
Bismuth(III) naphthenate	14	2
Dibutyltin(IV) dilaurate	37	8
None	0	0

DISCUSSION

Considerable evidence has been accumulated in favor of a ternary complex involving a rather loose association of the isocyanate, metal ion and the alcohol as the basis for the extreme catalytic activity of metal ions in isocyanate–hydroxyl reactions.

It is further evident that the metal-ion catalysis of isocyanate hydroxyl reactions is considerably enhanced by the presence of certain "activating" groups α or β (even γ) to the carbon carrying the reactive hydroxyl. Only very few metal ions (e.g., Mn^{+2}, Bi^{+3}, Bu_2Sn^{+2}) can significantly catalyze the isocyanate–n-butanol reaction.

In general the metal ion catalysts appear to fall into two groups: (1) catalysts which maintain a fair portion of their activity even in systems containing hindered isocyanates (e.g., Pb^{+2}, Bi^{+3}, Sn^{+2}), and (2) catalysts which are very sensitive to changes in steric factors at the isocyanate group (e.g., Co^{+2}, Zn^{+2}, Cd^{+2}). Apart from this there are several specific isocyanate–hydroxyl systems which are effectively catalyzed by metal ions generally inactive in other systems.

Recently Jones and Connor[4] have distinguished eight different classes of reactions involving metal-ion catalysis. If the only function of the metal ion is to bring the two reactants in closer proximity the catalysis is said to belong to class I. If the metal ion acts as an acid and through coordination increases the electrophilic character of a certain reactive site, then the catalysis is considered as belonging to class II.

Considering the metal-ion catalysis of the isocyanate–hydroxyl reaction it appears likely that the metal ion fullfils a twofold function: (1) it in-

creases the electrophilic character of the carbon in the isocyanate group by coordinating either at the oxygen or nitrogen, and (*2*) it brings both the isocyanate and the alcohol in closer proximity by forming a ternary complex.

Consequently this reaction seems to belong both to class I and II.

Based on the experimental results two mechanisms are proposed; one for a simple monofunctional alcohol, the other for the "activated" alcohol.

In the case of a monofunctional alcohol, the mechanism shown in scheme II is postulated.
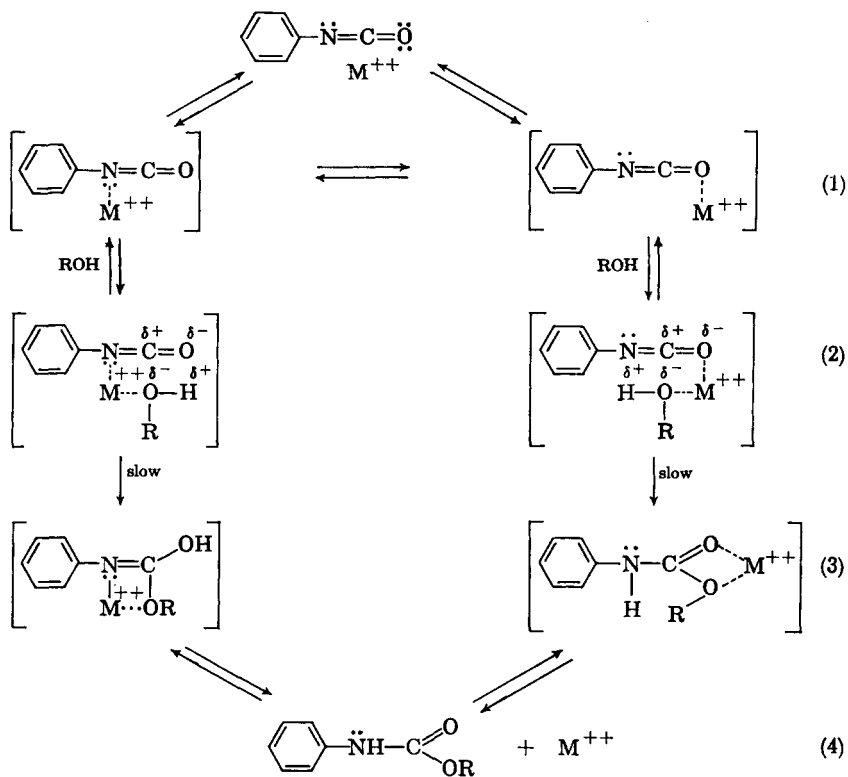
Scheme II

On the basis of this mechanism the metal ion catalysts would have to satisfy the following requirements: (*1*) they should possess a certain minimum complexing power in order to maintain a sufficient concentration of the ternary complex [equilibria (1) and (2)] to insure a rapid reaction; (*2*) on the other hand they should not destroy the nucleophilic character of the alcohol oxygen to such an extent as to render step (3) unlikely; (*3*) furthermore they should not complex tightly with the reaction product which would cause a removal of the metal ion from the reaction mixture [render step (4) unlikely].

Table X summarizes some of the data pertaining to the metal ions used

TABLE X

Instability Constant, Electronegativity, and Size of Metal Ions[a]

Ions	Electro-negativity	Size	$pK_{inst.}$[b]	$pK_{inst.}$[c]	$pK_{inst.}$[d]	$pK_{inst.}$[e]
Chromium(III)	1.6	0.70	17.8		<0	4.8
Manganese(II)	1.4	0.83	6		<0	—
Iron(III)	1.8	0.80	21.2	0	2.1	4.8
Cobalt(II)	1.5	0.72	4.6	3.5	<0	3.0
Nickel(II)	1.5	0.74	8.6	4.8	<0	1.7
Copper(II)	1.7	0.72	13.7	7.3	5.4	4.0
Zinc(II)	1.5	0.83	11.3	4.4	<0	—
Cadmium(II)	1.5	0.99	8.3	4.5	2.6	2.3
Indium(III)	1.8	—	19.8		1.5	3.6
Tin(II)	1.6	1.02	20.6		2.3	—
Antimony(III)	1.8	0.90	24.3		—	
Mercury(II)	1.9	1.05	22	17.5	13.2	17.5
Lead(II)	1.6	1.13	10.9		1.8	2.5
Bismuth(III)	1.8	1.20	15.8		4.7	2.3

[a] Data of Clifford.[5]

[b] For $M(OH)_2 \rightleftharpoons M(OH)^+ + OH^-$.

[c] For $M(NH_3)^{++}_2 \rightleftharpoons M(NH_3)^{++} + NH_3$.

[d] For $MCl_2 \rightleftharpoons MCl^+ + Cl^-$.

[e] For $M(NCS)_2 \rightleftharpoons M(NHS)^+ + SCN$.

as catalyst in this study as to their complexing power, electronegativity, and size.

These data can be used only as a guide since they apply to aqueous systems.

The complexing power of most metal ions (In^{+3}, Cr^{+2}, Fe^{+3}, Sn^{+2}, Sb^{+3}, etc.) used in this study is probably sufficient to satisfy requirement (1).

Requirement (2) would appear the hardest one to satisfy for systems containing monofunctional alcohols. Especially in the case of the more electronegative metal ions which are known to form bonds of considerable covalent character (Sn^{+2}, Hg^{+2}, Pb^{+2}) a monofunctional alcohol might lose most of its nucleophilicity necessary for reaction. Ions of lower electronegativity (Bi, Sn^{+2}, Mn^{+2}, Fe^{+3}) would form a more ionic bond which would allow the alcohol to retain a sufficient portion of its nucleophilicity and achieve fair reactivity. Bi^{+3} ion appears to be somewhat anomalous but it also is known to act contrary to its high electronegativity in other areas (e.g., amphoterism).

Some of the complexes probably involve predominantly nitrogen-metal ion coordination (Mn^{+2}, Bi^{+3}) since the catalytic activity is drastically decreased in systems containing sterically hindered isocyanates.

It seems possible that the inactivity of some metal ions (Cr^{+3}, In^{+3}) could be attributed to failure to satisfy requirement (3), because they complex rather strongly.

Another factor not mentioned before is the availability of at least two sites for complexing which would depend on the coordination number of the

metal ion and on the degree of ionization of this compound in the reaction medium.

In the case of an "activated" alcohol the mechanism postulated is shown in scheme III.

$$R—X—CH_2—CH_2—OH \tag{1'}$$

$$M^{++}$$

$$\begin{array}{c} M^{++} \\ R—\ddot{X} \quad \quad O—H \\ CH_2—CH_2 \end{array}$$

$$\text{(2')}$$

$$\begin{bmatrix} & N=C=O \\ H_3C & \vdots \\ R—X \quad M^{++} \quad O—H \\ CH_2—CH_2 \end{bmatrix} \rightleftharpoons \begin{bmatrix} & \ddot{N}=C=O \\ H_3C & \\ H—O \quad M^{++} \quad X—R \\ CH_2—CH_2 \end{bmatrix}$$

$$\text{(3')}$$

$$\begin{bmatrix} CH_3 \\ —N=C—OH \\ M^{++}\cdots O \\ R—X \quad \quad \\ CH_2—CH_2 \end{bmatrix} \qquad \begin{bmatrix} \ddot{N}H—C=O \\ CH_3 \quad O\cdots M^{++} \\ \quad X—R \\ CH_2—CH_2 \end{bmatrix}$$

$$\text{Product} + M^{++} \tag{4'}$$

Scheme III.

Introduction of another functional group α or β to the carbon atom carrying the reactive hydroxyl would be expected to change significantly the ability of the system to satisfy the above mentioned requirements in regard to each specific metal ion.

The "activating" group would be expected to exert the following influence.

It would increase the overall stability of the metal ion–alcohol complex [equilibrium (1)] as long as a five-, six-, or probably seven-membered chelate ring could be formed.

It would allow the hydroxyl to retain a larger portion of its nucleophilicity, especially in complexes containing the more electronegative metal ions.

However, it could also produce a urethane which would chelate rather strongly the metal ion and consequently kill the catalysis as more and more product is formed.

Finally, in the case where only two coordination sites were available, the alcohol could occupy both these sites and prohibit the formation of the ternary complex.

The evidence presented in Tables I, II, VII, and VIII clearly indicates the necessity for chelation, as almost all metal ions exhibit greater catalytic activity in systems containing 1,2- and 1,3-glycols as compared to systems containing 1-butanol, 1,4-glycol, or 1,5-glycol.

Especially significant appears to be the decrease in catalytic activity in systems containing hindered isocyanates.

Several of the metal ions suffer such a pronounced deactivation from the introduction of one o-methyl group in the phenyl isocyanate molecule that it is very hard to explain this behavior just on the basis of weakening the overall complex stability. Therefore it seems reasonable to postulate the formation of both oxygen and nitrogen coordinated isocyanate-metal ion complexes.

It appears that metal ions which are known to show special affinity for nitrogen (Cd^{+2}, Zn^{+2}, Cu^{+2}, Ni^{+2}) are particularly sensitive to increased steric hindrance at the isocyanate group.

This would also explain the behavior of Hg^{+2} which is a strong complexer, but has a special affinity for nitrogen (see Table X) and consequently suffers from steric sensitivity.

The sensitivity to steric hindrance however, increases in going from 1,2- to 1,5-glycols (Table XI), indicating that also the overall complex stability is a factor and that only chelation can increase the stability of the ternary complex sufficiently to produce the maximum catalytic effect.

TABLE XI
Steric Sensitivity of Sn^{+2}-Catalyzed Systems

	1-min. heat rise, °C.	
Glycol	Phenyl isocyanate	o-Tolyl isocyanate
1,2-Ethylene glycol	35	32
Neopentyl glycol	40	12
1,4-Butylene glycol	8	1
1,5-Pentanediol	5	1

On comparing the 1,2 activated alcohols (Tables III–VI) it becomes apparent that by changing the nature of the "activating" group in such a manner as to produce a more stable chelate an enhanced catalytic activity is observed for most metal ions. Furthermore, one would expect that by changing the nature of the "activating" group in such a manner as to form a more stable chelate the steric sensitivity of such a system would be decreased. (Table XII). This appears to be indicated in several instances, especially for Hg^{+2} and Sn^{+2} ions.
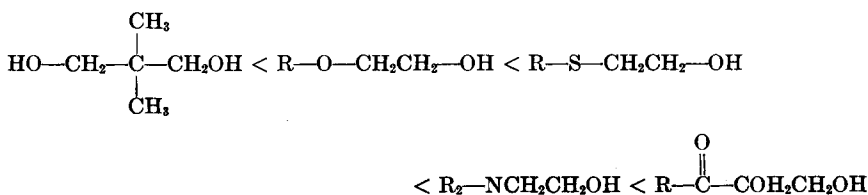
TABLE XII
Steric Effect in Hg^{+2}-Catalyzed Systems

	1-min. heat rise, °C.	
Alcohol	Phenyl isocyanate	o-Tolyl isocyanate
2-Hydroxyethyl acetate	18	6
2-Ethoxyethanol	20	5
2-Ethyl thioethanol	33	9
Ethylene glycol	35	11

Catalytic deactivation during the reaction becomes especially important in systems containing 2-hydroxyethyl acetate (Figs. 5 and 6). This can be explained in terms of increased product–metal ion chelate stability.

The order of deactivation for the various alcohols is the following:

$$\text{HO—CH}_2\text{—}\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{CH}_3}{|}}{\text{C}}}\text{—CH}_2\text{OH} < \text{R—O—CH}_2\text{CH}_2\text{—OH} < \text{R—S—CH}_2\text{CH}_2\text{—OH}$$

$$< \text{R}_2\text{—NCH}_2\text{CH}_2\text{OH} < \text{R—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—COH}_2\text{CH}_2\text{OH}$$

It is interesting to note the almost complete absence of deactivation (and in some cases even the presence of pronounced activation) of catalysis during the reaction for the neopentyl glycol–phenyl isocyanate system (Fig. 7). The fact that the system represents the only case in which a total heat rise of 40 °C. has been obtained indicates that the deactivation of the catalysts by the product is probably more important than previously anticipated.

References

1. Britain, J. W., and P. G. Gemeinhardt, *J. Appl. Polymer Sci.*, **4**, 207 (1960).
2. Smith, H. A., *J. Appl. Polymer Sci.*, **7**, 85 (1963).
3. Fischer, J. R., *Tetrahedron*, **19**, 97 (1963).
4. Jones, M. M., and W. A. Connor, *Ind. Eng. Chem.*, **55**, No. 9, 15 (1963).
5. Clifford, A. F., *Inorganic Chemistry of Qualitative Analysis*, Prentice-Hall, Englewood Cliffs, N. J., 1961.

Résumé

La catalyse par les ions métalliques des réactions isocyanate–hydroxyle est fortement améliorée par la présence de certains groupes activants en alpha, bèta ou même en gamma par rapport au carbone portant l'hydroxyle réactif. Peu d'ions métalliques peuvent catalyser d'une façon marquante la réaction isocyanate–butanol. En général, on peut diviser les catalyseurs ions métalliques en deux groupes: les catalyseurs qui conservent une assez grande partie de leur activité même dans les systèmes contenant des isocyanates empêchés stériquement et ceux qui sont très sensibles aux changements dans les

facteurs stériques.   On estime que les ions métalliques ont une double action: ils aug-
mentent le caractère électrophile de la fonction isocyanate par coordination avec l'oxy-
gène ou l'azote et ils permettent à l'isocyanate et à l'alcool d'être à proximité l'un de
l'autre.   On estime que les fonctions activantes possèdent deux effets contraires: ils
augmentent la stabilité globale du complexe ternaire tant en gardant le caractère nucléo-
phile de l'hydroxyle et ils produisent dans certains cas des uréthannes, qui de préférence
forment de chélates avec les ions métalliques et arrêtent la catalyse.   Tous les ions
métalliques ont une plus grande activité catalytique pour les systèmes contenant des
glycols 1,2 que pour ceux contenant des glycols 1,4.   De plus, la sensibilité vis-a-vis de
l'empêchement stérique augmente des glycols 1,2 à 1,4 ce qui indique qu'uniquement la
chélation peut augmenter d'une façon suffisante la stabilité du complexe ternaire et prod-
uire un effet catalytique maximum.

Zusammenfassung

Die Metallionenkatalyse der Isocyanat-Hydroxyreaktionen wird durch die Gegenwart
gewisser "aktivierender" Gruppen in α-, β- und sogar γ-Stellung zum Hydroxyl-tragen-
den Kohlenstoff beträchtlich verstärkt.   Wenige Metallionen können die Isocyanat-
Butanolreaktion in beträchtlichem Ausmass katalysieren.   Im allgemeinen gibt es zwei
Gruppen von Metallionenkatalysatoren: Katalysatoren, welche einen beträchtlichen
Teil ihrer Aktivität auch in Systemen mit gehindertem Isocyanat behalten und Kataly-
satoren, die gegenüber einer Änderung der sterischen Faktoren sehr empfindlich sind.
Es wird angenommen, dass die Metallionen eine doppelte Funktion erfüllen: Sie erhöhen
den elektrophilen Charakter der Isocyanatgruppe durch Koordination entweder an Sau-
erstoff oder an Stickstoff; ausserdem bewirken sie eine grössere Annäherung des Iso-
cyanats an Alkohol.   Die "aktivierenden" Gruppen scheinen zwei einander entgegenge-
setzte Haupteinflüsse zu haben: Sie erhöhen die Gesamtstabilität des ternären Kom-
plexes unter Beibehaltung des grössten Teils des nukleophilen Charakters der Hydroxyl-
gruppe und bilden in einigen Fällen Urethane, welche das Metallion bevorzugt chelieren
und die Katalyse vernichten.   Alle Metallionen zeigen in Systemen mit 1,2-Glycolen
grössere Katalysatoraktivität als in solchen mit 1,4-Glycolen, weiters nimmt die Emp-
findlichkeit gegen sterische Hinderung von 1,2- zu 1,4-Glycolen zu, was zeigt, dass nur
die Chelierung die Stabilität der ternären Komplexe genügend steigern kann, um einen
maximalen katalytischen Effekt zu erhalten.