

## Catalysis of the Isocyanate-Hydroxyl Reaction\*

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The reactions of aromatic isocyanates with various alcohols have been studied by several workers.<sup>1-4</sup> These investigations have shown that the relative reaction rates of alcohols are: primary alcohol > secondary alcohol > tertiary alcohol. By the use of appropriate catalysts it has been possible to increase the speed of the reactions between secondary hydroxyl groups and isocyanate groups to such a point that manufacture of one-shot polyurethane foam based on the secondary hydroxyl-containing polyoxypropylene triols and diols has been possible.

TABLE I

Catalyst Tests of Bismuth, Lead, Triethylenediamine, and Basic Compounds for the Isocyanate-Hydroxyl Reaction

Compound tested	Gelation time at 70°C., min.
Blank	>240
Bismuth nitrate	1
Lead 2-ethylhexoate (24% Pb) <sup>a</sup>	1
Lead benzoate <sup>a</sup>	8
Lead oleate <sup>a</sup>	4
Triethylenediamine	
(1,4-diaza-[2.2.2]-bicyclooctane)	4
Sodium trichlorophenate <sup>a</sup>	2
Sodium propionate <sup>a</sup>	32
Lithium acetate <sup>a</sup>	60
Potassium oleate <sup>a</sup>	10

<sup>a</sup> Isocyanate trimerization catalyst.

The studies of catalysis of the isocyanate-hydroxyl reaction<sup>1-3,5-10</sup> with a few exceptions<sup>11,12</sup> have been made with an isocyanate and an alcohol in a dilute solution. The reactions were followed by analysis for unreacted isocyanate. The authors wished to study the isocyanate-hydroxyl reaction catalysis in a system which more nearly represented the commercially available isocyanates and polyols for urethane polymers. Also it was desirable to use a method which would lend itself to large-scale screening of hundreds of potential catalysts.

The isocyanate selected for the screening tests

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was tolylene diisocyanate (80/20 ratio of 2,4/2,6 isomer mixture) and the hydroxyl compound was a secondary hydroxyl-containing polyoxypropylene triol. The two reactants were mixed in stoichiometric amounts in the presence of the catalyst to be tested and placed in a test tube in a constant temperature bath at 70°C. The tubes were observed to determine the time required for gelation of the reaction mixture. This gelation time was interpreted as a measure of the speed of the isocyanate-hydroxyl reaction in the mixture. The same weight of the compounds to be tested for catalytic activity was used in all tests. This greatly simplified the screening of so many different

TABLE II

Catalyst Tests of Stannous, Stannic, and Polyalkyl Tin Compounds for the Isocyanate-Hydroxyl Reaction

Compound tested	Gelation time at 70°C., min.
Tetrabutyltin	>240
Tributyltin chloride	200
Dibutyltin dichloride	109
Butyltin trichloride	4
Stannic chloride	3
Tributyltin <i>o</i> -phenylphenate	14
Tributyltin cyanate	5
Stannous octoate	4
Stannous oleate	8
Stannous tartrate	>240

TABLE III

Catalyst Tests of Dialkyltin Compounds for the Isocyanate-Hydroxyl Reaction

Compound tested	Gelation time at 70°C., min.
Dibutyltin di(2-ethylhexoate)	4
Dibenzyltin di(2-ethylhexoate)	5
Dibutyltin dilaurate	8
Dibutyltin diisooctylmaleate	4
Dibutyltin sulfide	20
Dibutyltin dibutoxide	3
Dibutyltin bis( <i>o</i> -phenylphenate)	3
Dibutyltin bis(acetylacetonate)	4
Di(2-ethylhexyl) tin oxide	3

compounds. Tables I-IX are part of the results of the catalyst screening of hundreds of compounds. All of the compounds which are listed in the tables were soluble in the reaction mixture used in the tests.

Some of the compounds tested are excellent trimerization catalysts for isocyanates; they are indicated by an asterisk in the tables. This side reaction could influence the observed gelation time and will be the subject of a future publication.

Many metallic compounds were found to be catalysts for the isocyanate-hydroxyl reaction. A

TABLE IV  
Catalyst Tests of Titanium and Iron Compounds for the Isocyanate-Hydroxyl Reaction

Compound tested	Gelation time at 70°C., min.
Titanium tetrachloride	50
Dibutyltitanium dichloride	13
Tetrabutyl titanate	8
Butoxytitanium trichloride	16
Ferric chloride	6
Ferric 2-ethylhexoate (6% Fe)	16
Ferric acetylacetonate	16
Ferrocene	>240

TABLE V  
Catalyst Tests of Antimony, Uranium, Cadmium, and Cobalt Compounds for the Isocyanate-Hydroxyl Reaction

Compound tested	Gelation time at 70°C., min.
Antimony trichloride	13
Antimony pentachloride	90
Triphenylantimony dichloride	30
Triphenylantimony	>240
Uranyl nitrate	25
Cadmium nitrate	180
Cadmium diethyldithiophosphate	30
Cobalt benzoate	32
Cobalt 2-ethylhexoate (6% Co)	12

TABLE VI  
Catalyst Tests, of Thorium, Aluminum, Mercury, Zinc, and Nickel Compounds for the Isocyanate-Hydroxyl Reaction

Compound tested	Gelation time at 70°C., min.
Thorium nitrate	32
Triphenylaluminum	32
Trioctylaluminum	32
Aluminum oleate	70
Diphenylmercury	40
Zinc 2-ethylhexoate (22% Zn)	65
Zinc naphthenate (14.5% Zn)	60
Nickelocene	50
Nickel naphthenate (6% Ni)	180

list of the type compounds in a roughly descending order of catalytic activity is: Bi, Pb, Sn, triethylenediamine, strong bases, Ti, Fe, Sb, U, Cd, Co, Th, Al, Hg, Zn, Ni, trialkyl amines, Ce, Mo, V, Cu, Mn, Zr, and trialkyl phosphines. Arsenic, boron, calcium, and barium compounds have not shown any catalytic activity within the limits of the screen-

TABLE VII  
Catalyst Tests of Tertiary Amine Compounds for the Isocyanate-Hydroxyl Reaction

Compound tested	Gelation time at 70°C., min.
1-Methyl-4-(dimethylaminoethyl)-piperazine	90
<i>N</i> -Ethylethylenimine	32
<i>N, N, N', N'</i> -Tetramethylethylenediamine	60
Triethylamine	120
2,4,6-Tri(dimethylaminomethyl)-phenol	50
<i>N</i> -Ethylmorpholine	180
2-Methylpyrazine	>240
Dimethylaniline	>240
Nicotine	240

TABLE VIII  
Catalyst Tests of Cerium, Molybdenum, Vanadium, Copper, Manganese, and Zirconium Compounds for the Isocyanate-Hydroxyl Reaction

Compound tested	Gelation time at 70°C., min.
Molybdenum hexacarbonyl	90
Cerium nitrate	85
Vanadium trichloride	90
Cupric 2-ethylhexoate (8% Cu)	120
Cupric acetate	90
Manganese 2-ethylhexoate (6% Mn)	120
Manganese linoresinate (8% Mn)	240
Zirconium 2-ethylhexoate (6% Zr)	240
Zirconium naphthenate (6% Zr)	240

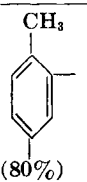
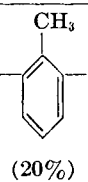
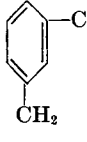
TABLE IX  
Catalyst Tests of Phosphorus, Arsenic, Boron, Calcium, and Barium Compounds for the Isocyanate-Hydroxyl Reaction

Compound tested	Gelation time at 70°C., min.
Triphenyl phosphine	240
Tributyl phosphine	>240
Trimethyl phosphite	>240
Triphenyl arsine	>240
Arsenic trichloride	>240
Boron trifluoride diethyl ether complex	>240
Pyridine boran	>240
Calcium acetate	>240
Barium acetate	>240

ing test used. The abnormally high catalytic activity of triethylenediamine in comparison to the other tertiary amines has been explained by Farkas and Flynn.<sup>9</sup> The tin compounds should be noted, in particular, the series of compounds: tetrabutyltin, tributyltin chloride, dibutyltin dichloride, butyltin trichloride, and stannic chloride. This regular increase in activity can be explained by steric hindrance of the butyl groups in the compounds.

Other workers<sup>5,6,13</sup> have shown the relative reaction rates of isocyanates with alcohols to be dependent upon the structure of the isocyanate. For example, the relative reaction rates for the reactions of three typical diisocyanates<sup>5,13</sup> are shown in Table X. The aliphatic isocyanates, when used in place of the aromatic isocyanates have shown less yellowing of the urethane products than their aromatic counterparts. However, the low reactivity of the aliphatic isocyanates has made it impractical to use them in most cases. The proper catalysts may make the use of aliphatic isocyanates more realistic.

TABLE X  
Reaction Rates of Three Different Diisocyanates

OCN—R—NCO + R'OH $\xrightarrow{k_1}$ OCN—R—NH—CO <sub>2</sub> R'		$k_1$	
OCN—R—NH—CO <sub>2</sub> R' + R'OH $\xrightarrow{k_2}$ R'O <sub>2</sub> C—NH—R—NH—CO <sub>2</sub> R'		$k_2$	
—R—		$k_1$	$k_2$
 (80%)	 (20%)	353	32
		23.2	21
—(CH <sub>2</sub> ) <sub>6</sub> —		1	0.5

Gelation tests similar to those described above with tolylene diisocyanate were carried out with *m*-xylylene diisocyanate and the same triol and also with hexamethylene diisocyanate and the triol. In these tests the order of strength of the catalysts was found to be different than when tolylene diisocyanate was used. Table XI lists the results of

some catalyst screening tests with the three different diisocyanates.

TABLE XI  
Catalyst Tests with Three Different Isocyanates

Compound tested	Gelation time (min.) at 70°C. with:		
	Tolylene diisocyanate	<i>m</i> -xylylene diisocyanate	Hexamethylene diisocyanate
Blank	>240	>240	>240
Triethylamine	120	>240	>240
Triethylenediamine	4	80	>240
Stannous octoate	4	3	4
Dibutyltin di(2-ethylhexoate)	6	3	3
Lead 2-ethylhexoate (24% Pb)	2	1	2
Sodium <i>o</i> -phenylphenate	4	6	3
Potassium oleate	10	8	3
Bismuth nitrate	1	1/2	1/2
Tetra(2-ethylhexyl) titanate	5	2	2
Stannic chloride	3	1/2	1/2
Ferric chloride	6	1/2	1/2
Ferric 2-ethylhexoate (6% Fe)	16	5	4
Cobalt 2-ethylhexoate (6% Co)	12	4	4
Zinc naphthenate (14.5% Zn)	60	6	10
Antimony trichloride	13	3	6

A list of the type compounds in decreasing order of catalytic activity for the aliphatic isocyanate-hydroxyl reaction is: Bi, Fe, Sn, Pb, Ti, Sb, strong bases, Co, Zn, triethylenediamine, trialkyl amines.

The catalysts tested can be classified into three groups. The first group, tertiary amine catalysts, do not greatly affect the relative reaction rates of the different isocyanates. The second group includes stannous, lead, bismuth, and organotin compounds which activate the aliphatic diisocyanates more than tolylene diisocyanate so that the relative rates of the diisocyanate reactions are approximately equal. Members of the third group have a much larger effect on the aliphatic diisocyanates so that these diisocyanates are faster to react with hydroxyl groups than tolylene diisocyanate. This last group includes zinc, cobalt, iron, stannic, antimony, and titanium compounds. An explanation of these observed effects can be found in an examination of the reaction mechanism. Baker, Gaunt, Davies, and Holdsworth<sup>1,7</sup> proposed the mechanism (1) for catalysis of the isocyanate-hydroxyl reaction by tertiary amines:



diisocyanate (9.4 g. per test) and also with hexamethylene diisocyanate (Mobay's Mondur HX, 8.4 g. per test).

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### Synopsis

The reaction of tolylene diisocyanate (80/20 mixture of 2,4 and 2,6-isomer) with a secondary hydroxyl-containing polyoxypropylene triol was studied in the presence of numerous compounds to test their catalytic effect on the reaction. The reaction was studied by determination of the gelation time of the reaction mixture. Many metallic compounds were found to be good catalysts for the isocyanate-hydroxyl reaction. Compounds in roughly descending catalytic activity are: Bi, Pb, Sn, triethylenediamine, strong bases, Ti, Fe, Sb, U, Cd, Co, Th, Al, Hg, Zn, Ni, trialkylamines, Ce, Mo, V, Cu, Mn, Zr, trialkyl phosphines. Similar gelation tests were made with *m*-xylene diisocyanate and the same triol and also with hexamethylene diisocyanate and the triol. In these tests the order of strength of the catalysts was found to be different than when tolylene diisocyanate was used.

In decreasing order of activity: Bi, Fe, Sn, Pb, Ti, Sb, strong bases, Co, Zn, triethylenediamine, trialkyl amines. A mechanism is proposed for the way in which a metal compound may catalyze the isocyanate-hydroxyl reaction. Steric hinderance is suggested to explain the differing catalytic activity observed with tolylene diisocyanate and the unhindered aliphatic diisocyanates.

### Résumé

La réaction du diisocyanate de toluène (mélange d'isomères 2,4/2,6 dans le rapport 80/20) avec le triol de polyoxypropylène contenant un groupe hydroxyle secondaire a été étudiée en présence d'un grand nombre de composés en vue de déterminer leur effet catalytique sur la réaction. La réaction a été étudiée par détermination du temps de gélification du mélange réactionnel. Plusieurs composés métalliques semblent être de bons catalyseurs pour la réaction isocyanate-hydroxyle. Les composés suivants présentent une activité catalytique décroissante: Bi, Pb, Sn, triéthylènediamine, les bases fortes, Ti, Fe, U, Cd, Co, Th, Al, Hg, Zn, Ni, trialkcoylamines, Ce, Mo, V, Cu, Mn, Zr, trialkcoylphosphines. Des essais similaires de gélification ont été effectués en employant le diisocyanate de *m*-xylène et le même triol, de même en utilisant le diisocyanate d'hexaméthylène et le triol. Dans ces essais, l'ordre des catalyseurs suivant leur force est différent de celui obtenu lorsqu'on utilise le diisocyanate de toluène. Nous avons dans un ordre d'activité décroissante: Bi, Fe, Sn, Pb, Ti, Sb, les bases fortes, Co, Zn, triéthylènediamine, trialkcoylamines. On propose un mécanisme pour expliquer la façon dont un dérivé métallique peut catalyser la réaction isocyanate-hydroxyle. On suggère un empêchement stérique pour expliquer les différentes activités catalytiques observées avec le diisocyanate de toluène et les diisocyanates aliphatiques exempts d'empêchement stériques.

### Zusammenfassung

Die Reaktion von Tolylendiisocyanat (80/20, 2,4/2,6-Isomerenmischung) mit einem sekundärhydroxyl-hältigen Polyoxypropylentriol wurde in Gegenwart zahlreicher Verbindungen untersucht, um deren katalytischen Einfluss auf die Reaktion zu prüfen. Die Reaktion wurde durch Bestimmung der Gelierungsdauer der Reaktionsmischung untersucht. Es wurde gefunden, dass viele Metallverbindungen gute Katalysatoren für die Isocyanat-Hydroxylreaktion sind. Ungefähr nach abnehmender katalytischer Wirksamkeit geordnet, ergibt sich die Reihenfolge der Verbindungen: Bi, Pb, Sn, Triäthylendiamin, starke Basen, Ti, Fe, Sb, U, Cd, Co, Th, Al, Hg, Zn, Ni, Trialkylamine, Ce, Mo, Va, Cu, Mn, Zr, Trialkylphosphine. Ähnliche Gelierungstests wurden mit *m*-Xylylendiisocyanat und dem gleichen Triol durchgeführt; ebenso mit Hexamethylen-diisocyanat und dem Triol. Bei diesen Tests war die Reihenfolge der Stärke der Katalysatoren verschieden von der bei Verwendung von Tolylendiisocyanat gefundenen. Nach abnehmender Wirksamkeit geordnet: Bi, Fe, Sn, Pb, Ti, Sb, starke Basen, Co, Zn, Triäthylendiamin, Trialkylamine. Ein Mechanismus für die Katalyse der Isocyanat-Hydroxylreaktion durch eine Metallverbindung wird vorgeschlagen. Zur Erklärung der bei Tolylendiisocyanat und den unbehinderten aliphatischen Diisocyanaten beobachteten unterschiedlichen katalytischen Aktivität wird das Auftreten einer sterischen Hinderung angenommen.

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