Organolead Compounds as Potential Catalysts for Making Polyurethane Foams*

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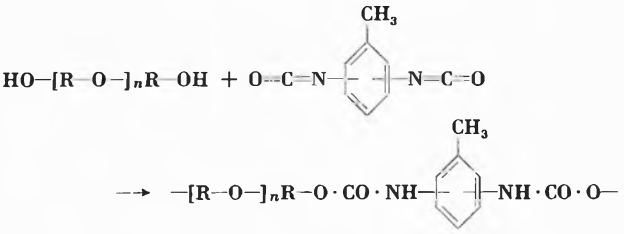
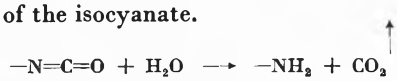
Polyether-urethanes are currently manufactured by reacting a linear or a branched polyether of moderate molecular weight with a polyfunctional isocyanate. The polyether component should carry terminal hydroxyl groups and optimally its molecular weight should lie between 2000 and 3000. Mostly an aromatic diisocyanate like tolylene diisocyanate is used as the reaction partner.



Essentially the same process can be used for the manufacture of foams. Then, however, the presence of a blowing agent is required. As such either a very volatile compound (like e.g. Freon) may be employed or carbon dioxide. The latter is formed if to the reaction components some water is added which then readily reacts with part of the isocyanate.



Of course, due precautions should be taken to ensure that the evolution of gas occurs when the polymerizing mass has the right viscosity, and also that the ultimate foam attains an even cell structure.

The reactions of the isocyanate both with the hydroxyl groups of the polyether component and with water proceed rather slowly. Therefore catalysts have to be added for both reactions, in particular if the process is to be conducted as a one-shot process. Actually, so far two separate catalysts are required, since each reaction needs its specific type of catalyst. At present, catalysis of the isocyanate-water reaction is usually effected by adding a tertiary amine such as 1,4-diaza-[2,2,2]-bicyclooctane (DABCO) or N-ethylmorpholine. On the other hand, in order to catalyze the isocyanate-polyol reaction usually either a semi-organic tin salt like stannous dioctoate is applied or an organotin compound derived from tetravalent tin as e.g. dibutyltin dilaurate.

Since for many years already our Institute has been actively engaged in exploratory research in the field of organometallic chemistry based on each of the three IVth main group metals Ge, Sn and Pb, we started a more directed investigation into the nature of the catalytic processes just mentioned. Parallel to it we undertook a broad screening of representatives of these three groups of organometallics for any catalytic activity in

* Paper presented at the Third Symposium "Makromolekulare Stoffe", Zürich, October 1964.

either reaction, paying special attention to the compounds containing Pb or Ge.

The outcomes of the latter screening program may be summarized briefly as follows:

1. Organolead compounds of a distinct type display a pronounced catalytic activity both in the isocyanate-hydroxyl and in the isocyanate-waterreaction;
2. None of the organogermanium compounds investigated showed any activity at all in either reaction;
3. Results with the organotin compounds are in accordance with data given in the literature.[1]

In 1960 BRITAIN and GEMEINHARDT[2] published some data on the catalysis of the isocyanate-hydroxyl reaction by salts of divalent lead with organic acids such as 2-ethylhexoic, benzoic and oleic acid. They had their compounds tested on a system comprising difunctional isocyanates and a polyoxypropylene triol. It was found that the semi-organic divalent lead salts are strong gelation catalysts. Besides, they had found that these salts also actively catalyse the trimerization of the isocyanate, an in the technical process undesired side-reaction. No data are given in their paper about any true organolead compounds (i.e. those with at least one carbon-lead bond), nor is mention being made about any catalytic effect on the isocyanate-water reaction.

The organolead compounds investigated by us have been taken from each of the four possible types of organoleads viz. R_4Pb, R_3PbX, R_2PbX_2 and $RPbX_3$, in which R represents an alkyl or aryl group and X either an inorganic element or group, or an organic radical bound to the lead atom by means of a hetero atom. Of the type $RPbX_3$ only aryl derivatives could be investigated, since the corresponding alkyl derivatives are too unstable to be isolated.

Since in the present screening program we wanted to get quickly an opinion about the potential applicability of the candidate compounds as catalysts in the technical process, we subjected the compounds to two test procedures, each of which imitates fairly closely one feature of the technical process.

As a first test we used a modification of the gelation test described by BRITAIN and GEMEINHARDT.[2]

In this test an intimate mixture (or a solution) of 1% by weight of the candidate catalyst with (in) a commercial branched polyether is carefully mixed at room temperature with a stoichiometric amount of tolylene diisocyanate (an 80/20 ratio of the 2,4-/2,6-isomer mixture). The time required for complete gelation at ambient temperature (absence of any flow when observed visually for about 1 minute) is used as a measure for the rate of the isocyanate-hydroxyl reaction.

As a second test we studied the influence of the candidate compounds on the reaction between tolylene diisocyanate and water. This test is a modified form of the gas evolution test described by WOLFE.[3]

In the latter test 1% by weight of the candidate catalyst is dissolved in 8 ml of a 1 : 1 mixture of tetrahydrofuran and dimethylcellosolve with 3% by weight of water. The reaction vessel, filled with carbon dioxide, is connected with a gas buret. Subsequently, a stoichiometric amount of tolylene diisocyanate is injected under vigorous stirring. The flask is carefully maintained at 30 °C. The time required for the formation of a definite amount of carbon dioxide (preferably about 35% of the theoretical amount) is used as a measure for the rate of the isocyanate-water reaction.

Table 1. Catalytic effect of organolead compounds on some isocyanate reactions

Type	Catalyst (conc. 1% by weight)	Gelation time in minutes	Time required for evolution of CO_2 in sec
–	none	> 360	> 600
R_4Pb	tetrabutyllead	> 360	> 600
	tetraphenyllead	> 360	> 600
R_3PbX	tributyllead acetate	360	170
	tributyllead laurate	> 360	180
	triphenyllead hydroxide	> 360	170
R_2PbX_2	dibutyllead dichloride	> 360	> 600
	dibutyllead dilaurate	> 360	430
	diphenyllead dilaurate	> 360	550
$RPbX_3$	phenyllead triacetate	9	15
	phenyllead tri*iso* butyrate	5	17
	phenyllead trilaurate	30	25
	phenyllead tri-2-ethylhexoate	35	37
	p-tolyllead triacetate	12	17
	β-naphthyllead triacetate	6	17
	β-naphthyllead tribenzoate	20	32
R_2SnX_2	dibutyltin dilaurate	32	178
SnX_2	stannous dioctoate	5	400
–	1,4-diaza-[2,2,2]-bicyclooctane (DABCO)		6
–	triethylamine		30

Some of the results obtained with both tests are summarized in table 1. For the sake of comparison the values obtained with some commercial catalysts are given as well.

The values given, upon comparison with the pertinent value of the blanc experiment, clearly indicate that none of the representatives of the types R_4Pb, R_3PbX or R_2PbX_2 show any or any significant activity in either test. In one respect this is a very remarkable result since it is well-known that the closely related organotins of the type R_2SnX_2 are active gelation catalysts, and actually are being used industrially.

It was a surprise to observe that in the lead series activity in the gelation test is restricted to the type with the lowest degree of substitution $RPbX_3$. Quantitatively, the catalytic activities of these compounds are similar to those found with organotins of the types R_2SnX_2 and $RSnX_3$.

The most striking observation, however, was that the present group of organoleads ($RPbX_3$) also are active

[1] See e.g. F. HOSTETTLER and E. F. COX, *Ind. Eng. Chem. 52* (1960) 609.

[2] J. W. BRITAIN and P. G. GEMEINHARDT, *J. Appl. Polymer Sci. 4* (1960) 207.

[3] H. W. WOLFE, *Foam Bulletin Du Pont de Nemours Nr. A-25495*, March 1960.

catalysts for the isocyanate-water reaction. This is completely in contrast with the situation with any of the organotins. Actually, hitherto none of the many semi-organic metal or organometallic compounds investigated had displayed such a strong catalytic effect in the gas evolution test.

The present findings suggest that it might be feasible to apply an organolead of the type $RPbX_3$ as the sole catalyst in the preparation of polyether-urethane foams i.e. without the simultaneous use of a tertiary amine as a foam catalyst. It largely depends on the relation between activity and concentration of the catalyst for either reaction whether this possibility may be realized. Only if a concentration can be found at which, under technical circumstances, the compound under investigation catalyzes either reaction to exactly the right extent, that compound may be applied as the sole catalyst. This possibility was verified experimentally.

A commercial branched polyether is intimately mixed in a cardboard beaker with 0.1 to 0.5% by weight of an aryllead triacylate, 3% of water and 1% of a commercial foam stabilizer. Subsequently, a stoichiometric amount of a tolylene diisocyanate isomer mixture is added under vigorous stirring. After about 15 seconds the mixture is transferred to a paper-lined mould which is isolated at the outside. After formation of the foam at ambient temperature, which usually occurs within one minute, the foam is allowed to attain complete gelation (about 10 minutes) and finally heated at 80 °C for another 10 minutes.

By this method foams have been obtained with a fine and regular foam structure and with densities varying from 0.02 to 0.04.[4]

None of the aryllead triacylates catalyze the trimerization of isocyanates as has been verified by the method of BRITAIN.[5]

[4] The procedure has been laid down in Dutch Patent Appl. No. 299.409 (October 18th, 1963) and in corresponding foreign applications.

[5] J. W. BRITAIN, *Ind. Eng. Chem.* (Prod. Res. & Dev.) *1* (1962) 261.

The technological merits of the present process and the chemical and mechanical properties of foams prepared by it are under investigation.

Acknowledgement

The organometallic compounds used in the present investigation have been made available by courtesy of the Germanium Research Committee, the Tin Research Council and the International Lead Zinc Research Organization. The authors are greatly indebted to Dr. SCHRADE F. RADTKE, Director of Research of the latter organization, for permission to publish these results.

The authors' thanks are due to Professor G. J. M. VAN DER KERK for his continous interest, to Dr. F. RIJKENS, Dr. J. G. A. LUIJTEN, Mr. L. C. WILLEMSENS and Dr. J. C. OVEREEM for their synthetic efforts and to Mr. A. VAN ELVEN for able assistance.

Zusammenfassung

Eine Reihe Organometallverbindungen, abgeleitet von den drei Vierte-Hauptgruppe-Metallen Germanium, Zinn und Blei, wurde geprüft auf etwaige katalytische Aktivität bei den beiden der Polyurethanschaumbildung zugrunde liegenden Teilreaktionen: die Isocyanat–Polyol- und Isocyanat–Wasser-Reaktion. Es wurden nur Verbindungen mit wenigstens einer Kohlenstoff–Metall-Bindung untersucht.

Unter den Organogermaniumverbindungen wurden gar keine katalytisch aktiven Repräsentanten aufgefunden.

Während in der Zinnreihe, wie auch von unseren Versuchen bestätigt wurde, namentlich Verbindungen des Strukturtypus R_2SnX_2 und $RSnX_3$ in der Isocyanat–Polyol-Reaktion Aktivität aufweisen und erstgenannte tatsächlich im technischen Schaumprozeß Verwendung finden, wurde überraschenderweise gefunden, daß in der Bleireihe nur Vertreter vom Typus $RPbX_3$ katalytisch aktiv sind. Überdies zeigte sich, daß die letztgenannte Verbindungsgruppe nicht nur die Isocyanat–Polyol-Reaktion, sondern auch die Isocyanat–Wasser-Reaktion katalysiert.

Schaumversuche zeigten, daß Organobleiverbindungen vom Typus $RPbX_3$ sich als Katalysatoren zur Herstellung von Polyurethanschäumen eignen. Dieses Verfahren hat das besondere Merkmal, daß kein tertiäres Amin als Kokatalysator mitverwendet werden muß.