

Catalytic properties of $\text{Fe}(\text{acac})_3$ and $\text{Cu}(\text{acac})_2$ in the formation of urethane from a diisocyanate derivative and EtOH

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Abstract

The catalytic performance of metal- β -diketone complexes $\text{Fe}(\text{acac})_3$ and $\text{Cu}(\text{acac})_2$ is described for urethane formation reactions from hexamethylene diisocyanate (HDI) and ethanol. This is a model reaction for the synthesis of polyurethane resin that takes place during the application of reactive paint. The best results are obtained for the reaction between HDI and EtOH catalysed by the $\text{Fe}(\text{acac})_3$ complex. The diurethane adduct selectivity is 90% with a turnover rate of 74 h^{-1} . Similar experiments conducted with a commercial catalyst, dibutyltin dilaurate (DBTDL), show that for the same reaction conditions no diurethane adduct is formed and that the turnover rate is lower (29 h^{-1}). © 1998 Elsevier Science B.V.

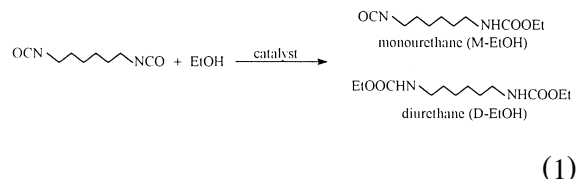
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1. Introduction

The catalytic formation of urethanes by addition of alcohols to isocyanates is a well known technological process. It represents one of the main routes in obtaining polyurethane products. The synthesis of polyurethane is based on the reaction between one or more isocyanate groups of a same molecule and an hydroxy group of alcohol molecules. Various metallic compounds are used as catalyst for this reaction and metal- β -diketones ($\text{M}(\text{acac})_n$) are often mentioned [1,2].

The catalytic behaviour of metallic complexes has been already described for model

reactions involving monoisocyanate and monoalcohol molecules [3,4]. We herein describe the study of the catalytic formation of urethanes by reaction between a hexamethylenediisocyanate (HDI) and ethanol (EtOH) (Eq. (1)) to mimic the complexity of the reaction between polyfunctional isocyanate and polyhydroxylated compounds founded in industrial processes.



The efficiency of $\text{Fe}(\text{acac})_3$ and $\text{Cu}(\text{acac})_2$ complexes is compared to the performances of cata-

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lysts used in industrial polyurethanes resins production: dibutyltin dilaurate (DBTDL) and zinc octanoate ($\text{Zn}(\text{oct})_2$). The activity and diurethane selectivity values obtained for these catalysts can give information about the cure time and the crosslinking degree of the resin, which are the main parameters for their coating applications.

2. Experimental

All manipulations were performed using standard Schlenk tube techniques under dry argon. The solvent and reagents were distilled over adequate desiccant agents. The acetylacetonate complexes, $\text{M}(\text{acac})_n$ ($\text{M} = \text{Fe}$ and Cu) were prepared following the procedures described in the literature [5,6]. The catalysts DBTDL ($\text{Bu}_2\text{Sn}(n\text{-C}_{11}\text{H}_{23}\text{CO}_2)_2$) and $\text{Zn}(\text{oct})_2$ were obtained from commercial sources and were used as received without further purification.

The catalytic reactions were performed under an argon atmosphere in a 70 ml glass reactor with magnetic stirring. In a typical experiment 50 ml of dichloromethane and 2.5 ml of the catalyst solution (9.1×10^{-3} mmol of metallic complex) were charged into the reactor and the

solution was heated to $30.0 \pm 0.5^\circ\text{C}$ (the temperature was controlled by an external circulation bath). Naphthalene was introduced as an internal standard (molar ratio HDI/naphthalene = 2.0) and then 1.78 mmol of isocyanate substrate–HDI (ratio HDI/catalyst = 200) were added, followed by 17.8 mmol ethanol (molar ratio ethanol/HDI = 10). After the addition of the alcohol, a sample was taken to perform the zero time analysis. Additional samples were taken at specific times and analysed by gas chromatography (HP 5890-A apparatus equipped with flame ionisation detector and a polydimethylsiloxane capillary column ($l = 30$ m, i.d. = 0.25 mm, film thickness = 0.2 μm)). The behaviour of the catalysts was evaluated on the basis of the turnover number obtained from the data determined by gas chromatography.

3. Results and discussion

3.1. Influence of the nature of the catalyst on the activity

Fig. 1 and Table 1 show the performance data of the reaction between HDI and EtOH in the presence of different metal catalysts. The

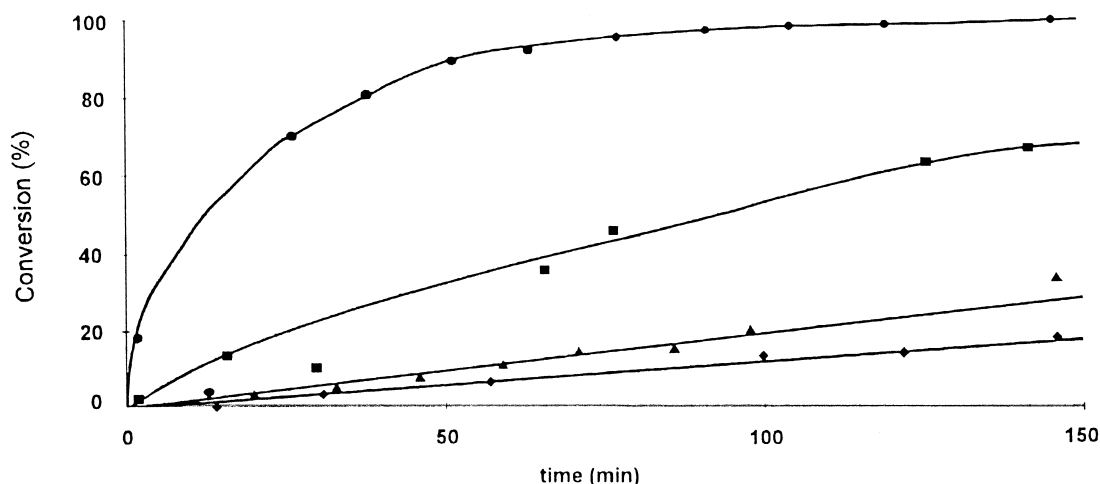


Fig. 1. Conversion of HDI in the reaction with EtOH in the presence of $\text{Fe}(\text{acac})_3$ (●), $\text{Cu}(\text{acac})_2$ (▲), DBTDL (■) and $\text{Zn}(\text{oct})_2$ (◆); $T = 30^\circ\text{C}$, molar ratio EtOH/HDI = 10; molar ratio HDI/cat. = 200.

conversion and turnover values were determined at a reaction time of 150 min. Without a catalyst there was no formation of urethane products. An experiment performed without a catalyst showed the beginning of reaction product formation only after three days.

Under our reaction conditions, the two β -diketone complexes showed activity in urethane production, the more active catalyst being $\text{Fe}(\text{acac})_3$ (entry 2, Table 1). It is worth noting that $\text{Fe}(\text{acac})_3$ is more than twice more active than the commercial catalyst, DBTDL (entries 2 and 5). Fig. 1 shows that the iron catalyst reached a high conversion (> 90%) after only ca. 50 min and attained total conversion after 125 min whereas the commercial catalyst, DBTDL, showed 66% conversion after 150 min.

3.2. Influence of the nature of the catalyst on the selectivity results

The reaction between HDI and EtOH gives monourethane (M-EtOH) and/or diurethane (D-EtOH). Table 2 shows selectivity in diurethane (S_D) and the conversions as a function of reaction time. With zinc catalyst the conversion observed was lower than 4% and only monourethane products were identified under these reaction conditions. With the copper catalyst, higher conversions of HDI were obtained (35% at 176 min) together with 4% of diurethane products. Catalysts which show higher conversion values ($\text{Fe}(\text{acac})_3$ and DBTDL) after 1 h of reaction time lead to the formation of

Table 1

Turnover and HDI conversion values for the catalytic reaction of HDI with EtOH^a

Catalyst	Turnover (h^{-1})	HDI conversion (%)
—	0.0	0.0
$\text{Fe}(\text{acac})_3$	74.2	99.5
$\text{Cu}(\text{acac})_2$	18.0	27.5
DBTDL	29.5	65.7
$\text{Zn}(\text{oct})_2$	3.6	14.3

^aReaction conditions: $T = 30^\circ\text{C}$, molar ratio EtOH/HDI = 10; molar ratio HDI/cat. = 200.

Table 2

Diurethane selectivity^a, S_D (%) and HDI conversion, C (%), as a function of time for the catalytic reaction of HDI to EtOH^b

Time (min)	$\text{Fe}(\text{acac})_3$		$\text{Cu}(\text{acac})_2$		DBTDL		$\text{Zn}(\text{oct})_2$	
	S_D	C	S_D	C	S_D	C	S_D	C
27	32	69	0	0	0	1	—	—
64	65	94	—	—	—	—	—	—
66	—	—	0	12	18	34	0	3
100	—	—	0	18	33	44	—	—
105	99	99	—	—	—	—	0	3
126	100	100	—	—	—	—	—	—
159	100	100	—	—	41	68	0	3
161	100	100	—	—	—	—	—	—
165	100	100	4	34	—	—	—	—
176	100	100	4	35	42	68	—	—
200	100	100	—	—	49	68	0	4.0

^aMonourethane selectivity ($S_M = 100 - S_D$).

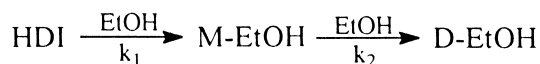
^bReaction conditions: $T = 30^\circ\text{C}$; molar ratio EtOH/HDI = 10; molar ratio HDI/cat. = 200.

—: No analysis has been done.

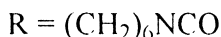
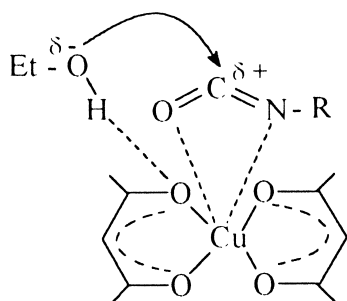
appreciable amounts of diurethane. Comparing $\text{Cu}(\text{acac})_2$ and DBTDL, for the same conversion of 34%, it is clear that DBTDL catalyst was more selective in diurethane ($S_D = 18\%$) than $\text{Cu}(\text{acac})_2$ ($S_D = 4\%$). Comparing also the same conversion of 68% tin complexes, DBTDL catalyst is more selective in diurethane products ($S_D = 48\%$) than $\text{Fe}(\text{acac})_3$ ($S_D = 32\%$). These results show that the selectivity is not only dependent on the conversion but also on the reaction mechanism involved.

3.3. Kinetic study

Under our reaction conditions the alcohol EtOH was in excess with respect to HDI (molar ratio EtOH/HDI = 10), allowing us to consider a pseudo-first order reaction [4]. The reaction between HDI and EtOH is described as a succession of two stages. The first stage leads to monourethane and the second competing with the first one leads to diurethane. Each stage can



Scheme 1.



Scheme 2.

be characterised by the respective kinetic constants k_1 and k_2 as shown in Scheme 1.

The kinetic constants obtained are shown in Table 3. The iron catalyst showed higher rate constants and was 6 times more active than the tin catalyst in relation to the first stage and 3.7 times more active in relation to the second stage.

The selectivities described in Section 3.2 can be explained by the values of $(k_1)_{\text{obs}}$ and $(k_2)_{\text{obs}}$. For both the iron and tin catalyst $(k_2)_{\text{obs}}$ was higher than $(k_1)_{\text{obs}}$. However for DBTDL the ratio $(k_2)_{\text{obs}}/(k_1)_{\text{obs}}$ was 7.5 which is higher than that for $\text{Fe}(\text{acac})_3$ ($(k_2)_{\text{obs}}/(k_1)_{\text{obs}} = 4.5$). These values imply that $\text{Fe}(\text{acac})_3$ and DBTDL are selective in diurethane products and that DBTDL is more selective in diurethane than the iron catalyst, as already mentioned in Section 3.2. The selectivity in diurethane obtained by $\text{Fe}(\text{acac})_3$ is due to its high activity leading to the total conversion of HDI into diurethane.

This kinetic study also corroborates the selectivity results of $\text{Cu}(\text{acac})_2$ and $\text{Zn}(\text{oct})_2$ which lead essentially to monourethane products. As the conversion of HDI was low, the concentration of HDI was higher than the monourethane

Table 3

Values of the kinetic constants $(k_1)_{\text{obs}}$ and $(k_2)_{\text{obs}}$ for the catalytic reaction of HDI to EtOH^a

Catalyst	$(k_1)_{\text{obs}}$ (10^{-3} min^{-1})	$(k_2)_{\text{obs}}$ (10^{-3} min^{-1})	$(k_2)_{\text{obs}}/(k_1)_{\text{obs}}$
$\text{Fe}(\text{acac})_3$	42.0 ± 0.5	190 ± 5	4.5
$\text{Cu}(\text{acac})_2$	7.15 ± 0.08	5.7 ± 0.2	0.8
DBTDL	7.18 ± 0.09	52 ± 2	7.2
$\text{Zn}(\text{oct})_2$	1.10 ± 0.01	1.0 ± 0.1	0.9

^aReaction conditions: $T = 30^\circ\text{C}$; molar ratio EtOH/HDI = 10; molar ratio HDI/cat. = 200.

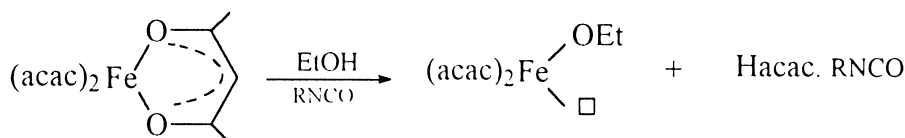
one. The ratio $(k_2)_{\text{obs}}/(k_1)_{\text{obs}}$ being inferior or equal to unity means the conversion of HDI to monourethane is much more important than the conversion of monourethane to diurethane. This concentration effect leads to a monourethane selectivity.

3.4. Mechanisms discussion

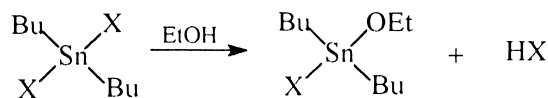
All results show a high activity of iron and tin catalysts in the reaction of HDI with EtOH when compared with the copper and zinc catalysts. This behaviour is probably due to the different active species responsible for the catalysis of the urethane formation.

Work published by Lipatova et al. [3] about the reaction between phenylisocyanate and methanol catalysed by the $\text{Cu}(\text{acac})_2$ complex showed that the coordination of the HDI to the metal is achieved via the oxygen and nitrogen atoms. The EtOH molecule interacting through a hydrogen bond with the oxygen atom of acetylacetonate ligand is converted to urethane by a nucleophilic attack on the coordinated diisocyanate molecule (Scheme 2).

On the $\text{Fe}(\text{acac})_3$ complex there is no vacant orbital to coordinate a HDI molecule. The activation of the EtOH molecule by the hydrogen bond with the oxygen atom of the acetylaceto-



Scheme 3.



Bu = C₄H₉

X = CH₃(CH₂)₁₀COO

Scheme 4.

nate ligand cannot explain the higher activity of this iron acetylacetonate complex compared to the copper one. In this way the interaction of EtOH with the Fe(acac)₃ could provide a vacant site on the metal probably via the elimination of acetylacetonate which reacts with the isocyanate [1] and the formation of an iron ethoxy species (Scheme 3). The alkoxy moiety should display a superior nucleophilicity compared to ethanol than permitting a more efficient attack to HDI.

Results reported by Houghton and Mulvaney [7] who studied the reactivity of phenyl isocyanate with butanol catalysed by DBTDL, showed that the active species is a metal–alkoxy complex formed by the coordination of the alcohol to the tin complex. Based on the activity of DBTDL for the studied reaction we propose that a similar species could be responsible for the activity of DBTDL (see Scheme 4).

Without the bibliography data on the reaction mechanism of Zn(oct)₂ for the studied system

and assuming that the structures of Zn(oct)₂ and Cu(acac)₂ are similar we could propose that these two catalysts present similar active species. Moreover the low activity of the zinc catalyst could indicate also that no alkoxy compound is formed.

The formation of a metal–alkoxy complex probably in the case of Fe(acac)₃ and in the case of DBTDL could explain their best activities compared to the copper and zinc catalyst.

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