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Influence of the alcohol nature on the catalytic properties of Fe(acac)$_3$ and Cu(acac)$_2$ in the formation of urethane from a diisocyanate

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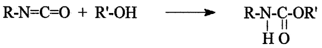
Abstract

The effect of the nature of alcohol, namely ethanol (EtOH), hydroxyethyl propionate (EPOH) and 2-hydroxypropyl propionate (PPOH), on the catalytic properties of Fe(acac)$_3$ and Cu(acac)$_2$ is evaluated in the formation of mono- and diurethanes from hexamethylenediisocyanate (HDI). The highest turnover rate,77 h^{-1}, was observed with the reaction between HDI and PPOH catalysed by Fe(acac)$_3$, which also afforded a diurethane selectivity of 100%. 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 (19 h^{-1}). A discussion concerning the probable active species is made in order to explain the activity, kinetic and selectivity results. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Urethanes; Hexamethylenediisocyanate; Metal–β-diketone complexes

1. Introduction

Industrial paint is obtained through a cure process in which one or various isocyanate groups of a diisocyanate or polyisocyanate react with a hydroxyl group of polyhydroxylated compounds as polyester, polyether or polyacrylate. Aliphatic isocyanates are less reactive than their aromatic analogues although they offer some advantages, such as better color retention and suitability for exterior applications. In order to overcome their low reactivity, a catalyst is employed to reduce the cure time. The choice of the polyhydroxylate compounds resides in properties such as film resistance. For instance, polyethers are used when the paint should be water-resistant, while polyacrylates lend an aesthetic finish [1]. We previously studied the catalytic formation of urethanes from the reaction between hexamethylenediisocyanate (HDI) and ethanol (EtOH) as a model of the complex reaction between polyfunctional isocyanate and polyhydroxylate compounds found in industrial process [2]. We describe herein studies relating to the influence of the nature of the alcohol on the catalytic cure of HDI.



$$\text{R-N=C=O} + \text{R'-OH} \longrightarrow \underset{\text{H}}{\text{R-N}}\text{-}\underset{\text{O}}{\overset{}{\text{C}}}\text{-OR'} \qquad (1)$$

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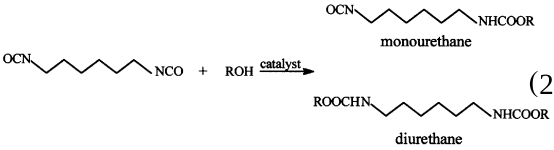
The addition of an R′OH molecule to an isocyanate function of a R—N═C═O compound takes place through a nucleophilic attack (Eq. 1). An electron-withdrawing R group favors this addition, since the positive charge of the carbonyl carbon is increased, facilitating the nucleophilic attack by the alcohol [3]. Moreover, the nature of the R′ group of the alcohol can also influence the nucleophilic attack. We have compared the properties of a primary alcohol such as hydroxyethyl propionate (EPOH), $C_2H_5COOCH_2CH_2OH$, to a secondary alcohol such as 2-hydroxypropyl propionate (PPOH), $C_2H_5COOCH_2CH(CH_3)OH$, and a small chain primary alcohol, EtOH, when using $Fe(acac)_3$, $Cu(acac)_2$ and dibutyltin dilaurate (DBTDL) as catalyst for the urethane formation. The efficiency of the iron and copper catalysts are compared to the industrial catalyst (DBTDL) through the evaluation of their activity and selectivity.

2. Experimental

All manipulations were performed using standard Schlenk tube techniques under dry argon. Solvents and reagents were distilled over the appropriate desiccant agents. The acetylacetonate complexes, $M(acac)_n$ (M = Fe and Cu) were prepared following the procedures already reported [4,5]. DBTDL, ($Bu_2Sn(n\text{-}C_{11}H_{23}\text{-}CO_2)_2$) was obtained from commercial sources and was used as received without further purification. EPOH and PPOH were obtained by hydrogenation of the double bonds of 2-hydroxyethyl acrylate and 2-hydroxypropyl acrylate, respectively, catalyzed by palladium over charcoal (hydrogen pressure: 50 atm, room temperature). Purities greater than 99% were confirmed by H^1-RMN. The catalytic reactions were performed and analyzed following the experimental conditions already described [2]. The behavior of the catalyst was evaluated on the basis of the turnover frequency, conversion and selectivity (S_D means selectivity towards diurethane).

3. Results and discussion

Table 1 reports turnover frequency (TOF), conversion (C) and selectivity (S_D) data determined after a reaction time of 50 min. The reaction between HDI and alcohols generates monourethane and/or diurethane (Eq. 2).



(2)

Without catalyst, under our experimental conditions, there is no urethane formation. An experiment performed without catalyst showed that urethane formation began only after 3 days.

Figs. 1–3 show the conversions of HDI vs. time when EtOH, EPOH and PPOH are used in the presence of $Fe(acac)_3$, DBTDL and $Cu(acac)_2$, respectively.

Table 1

Turnover frequency (TOF), HDI conversion (C) and diurethane selectivity (S_D), for the catalytic reaction of HDI with alcohols EtOH, EPOH and PPOH

Conditions: $T = 30°C$; molar ratio alcohol/HDI = 10; molar ratio HDI/catalyst = 200; reaction time = 50 min.

Catalyst	$Fe(acac)_3$			Cu $(acac)_2$			DBTDL		
Alcohol	EtOH	EPOH	PPOH	EtOH	EPOH	PPOH	EtOH	EPOH	PPOH
TOF (h^{-1})	216	72	77	29	41	6	77	17	19
C (%)	90	30	32	10	17	2	32	5	7
S_D (%)	52	100	100	0	100	100	11	100	0

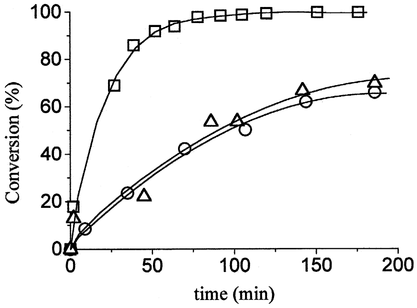


Fig. 1. Conversion of HDI in the reaction with alcohols EtOH (□), EPOH (○) and PPOH (△) in the presence of $Fe(acac)_3$.

From conversion data vs. time (Figs. 1 and 2) and activity results (TOF values, Table 1) one observes that the iron and tin catalysts, when associated to EPOH and PPOH, show the same behavior. For both, the activity and conversion order, in relation to the nature of the alcohol, is EtOH > PPOH ≈ EPOH. If the activity was correlated to a steric hindrance effect, one could expect similar results for EtOH and EPOH and different from what should be obtained with PPOH (secondary alcohol) as EtOH and EPOH are both primary alcohols [3]. As (i) the activity obtained with these two catalysts, when associated with EtOH, is largely superior to the activity obtained when EPOH is used and (ii) no expressive difference is noticed due to the use of EPOH or PPOH, we deduce that a steric hindrance effect cannot explain the activity data of iron and tin catalysts. As the activity for EPOH and PPOH is similar and low compared to EtOH, one can propose that there is an influence of the ester group of these alcohols in the formation of the active species. An interaction between the ester group and the metal probably exists, hindering the approach of the isocyanate reactant and thereby affecting the catalytic activity. As the behavior of the iron and tin catalyst with EPOH and PPOH are similar, one deduces that the CH_3 group of PPOH does not induce modification of the activity and conversion compared to the behavior of EPOH. One can say that the electronic effect of the CH_3 group that could lead to a higher nucleophilicity of the OH group of PPOH is probably compensated by a steric hindrance effect.

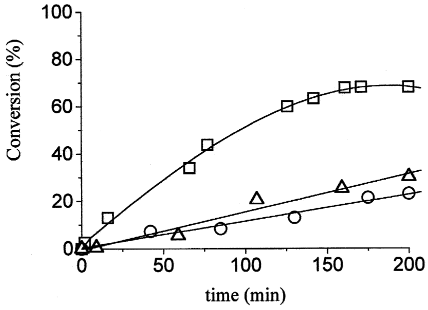


Fig. 2. Conversion of HDI in the reaction with alcohols EtOH (□), EPOH (○) and PPOH (△) in the presence of DBTDL.

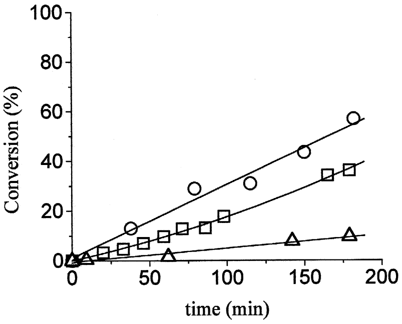


Fig. 3. Conversion of HDI in the reaction with alcohols EtOH (□), EPOH (○) and PPOH (△) in the presence of $Cu(acac)_2$.

Considering the copper catalyst (Table 1 and Fig. 3), this study shows that the highest conversion and turnover values are obtained when EPOH is used. The activity order correlated with the nature of the alcohol is EPOH > EtOH ≫ PPOH. The difference in behavior observed for the copper catalyst compared to the iron and tin catalysts lead us to suppose that the active species in the case of $Cu(acac)_2$ has different characteristics. In this case, one supposes that the ester group of EPOH and PPOH does not affect the catalytic species in the same way, as will be discussed later.

To elucidate the influence of the catalyst and nature of the alcohol on the urethane formation from HDI, we undertook a study of the kinetic aspects of our systems. Under our reaction conditions the alcohol (EtOH, EPOH or PPOH) is in excess with respect to HDI (molar ratio alcohol/HDI = 10). Under these conditions, we assume that the reaction is pseudo first-order reaction [8,9]. We have previously shown [2] that in the case of the formation of urethane catalyzed by Fe(acac)$_3$, Cu(acac)$_2$ and DBTDL from the HDI/EtOH system, monourethane and diurethane are produced and the selectivity changes with the reaction time. For kinetic studies, we have divided the reaction in two steps. The first one leads to the generation of monourethane and the second one corresponds to the monourethane coordination to the catalytic species leading to diurethane formation. Each step has been characterized through a kinetic constant. In the present study, the selectivity results (Table 1) show that the reaction between HDI and EPOH or PPOH alcohols leads to a unique product (monourethane or diurethane). Further studies show that these selectivities are independent of the reaction time. The reaction can then be characterized through a unique kinetic constant reported in Table 2. In order to evaluate the effect of the nature of the alcohol on the kinetics of the reaction, we also report on Table 2 the kinetic values for the HDI/EtOH system from the literature [2]. In this case, we report the kinetic constant of the second step of the reaction that corresponds to the diurethane formation and that attains the highest value when the catalyst is Fe(acac)$_3$ or DBTDL or in the case of Cu(acac)$_2$, is equal to the constant value of the first step.

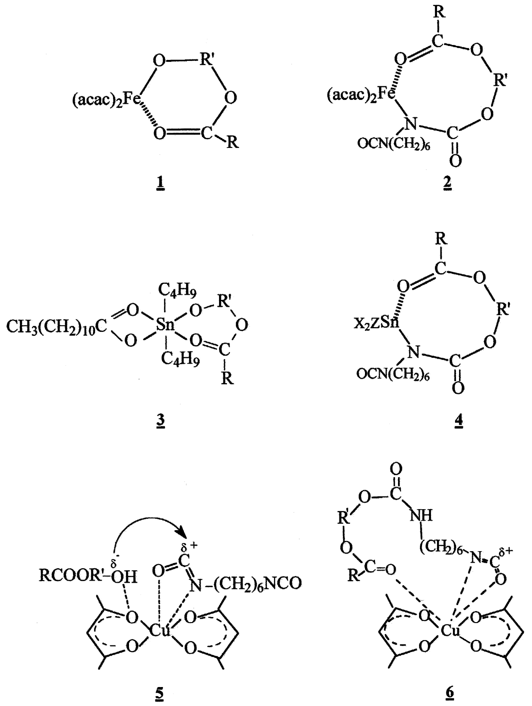
Table 2
Value of the observed kinetic constant k (10^{-3} min^{-1}) for the catalytic reaction of HDI with alcohols EtOH, EPOH and PPOH Conditions: $T = 30$°C; molar ratio alcohol/HDI = 10; molar ratio HDI/catalyst = 200.

Catalyst	k^{a}_{EtOH}	k_{EPOH}	k_{PPOH}
Fe(acac)$_3$	190 ± 5	6.5 ± 0.4	6.9 ± 0.5
Cu(acac)$_2$	2.6 ± 0.2	4.2 ± 0.5	0.50 ± 0.06
DBTDL	52.0 ± 0.2	1.4 ± 0.2	2.2 ± 0.3

[a] Reported kinetic constant of the second step of the reaction that corresponds to the diurethane formation [2].

The kinetics results confirm the observations from activity and conversion results. The order of the kinetic constants is similar for the iron and the tin catalyst: $k_{EtOH} \gg k_{EPOH} \cong k_{PPOH}$. These results corroborate the existence of an interaction of the ester group of EPOH and PPOH with the metal species proposed after the discussion of activity and conversion data. In the case of the copper catalyst, the order of the kinetic constants is $k_{EPOH} > k_{EtOH} > k_{PPOH}$ following the conversion and activity order mentioned above. These results confirm that the ester group of the EPOH and PPOH do not influence the catalytic species in the same way as for iron and tin. Based on activity, conversion and kinetics discussions, we can propose, for each catalyst, a structure of the active species responsible for the catalytic behavior.

In a previous study, we reported results on the urethane formation from the HDI/EtOH system catalyzed by Fe(acac)$_3$, DBTDL and Cu(acac)$_2$. In that case, we proposed that the similar catalytic behavior of the iron and the tin catalysts was due to an active species resulting from the coordination of the alcohol molecule and leading to an alkoxy moiety. Based on these previous results [2] and on the work reported by Houghton and Mulvaney [10] we propose, in this work (with variation of the nature of the alcohol), that the same kind of species is formed. Scheme 1 shows the alkoxy species (***1***) and (***3***) formed from the iron and tin catalysts when EPOH and PPOH are involved. The coordination of the alcohol enables the interaction of the ester group with the metal. In the case of the iron catalyst, a vacant site favors this kind of interaction. In the case of the tin catalyst, based on the literature [10,11] we propose that a hexacoordinated species is formed. The bidentate laurate carboxylate (Z) group and the ester group of the alcohol are coordinated to the tin (**3**). The coordination of the ester group in **1** and **3** renders the approach of the HDI molecule difficult, explaining the decrease in activity for the iron and the tin catalyst when associated with EPOH and PPOH. When EtOH is used, this



R = Et- ; **R'** = -CH_2CH_2- or -$CH(CH_3)$-CH_2-

X = C_4H_9- ; **Z** = $CH_3(CH_2)_{10}COO$-

Scheme 1.

kind of interaction does not exist, facilitating the coordination of HDI and leading to a highest activity, confirmed by the data in Table 1.

As we have already proposed for the $Cu(acac)_2$ catalyst [2], the catalytic species does not present interaction with the ester group. In this case, the alcohol molecule interacts through a hydrogen bond with the oxygen atom of the acetylacetonate ligand (Scheme 1, **5**) as already described [2]. This interaction allows HDI to be in closer proximity to the alcohol molecule around the catalytic species and then enables the nucleophilic attack. If this interaction is very strong, such a stabilization can affect the catalytic moiety leading to a decrease in activity. Since EtOH is a small molecule and has a more nucleophilic alcohol function compared to EPOH, we propose that the interaction of EtOH with the metallic species is greater than that observed with EPOH and the copper moiety leading to a more stable moiety. This stabilization effect, which decreases the nucleophilicity of the oxygen bound to hydrogen, can explain why $Cu(acac)_2$ is more active with EPOH than with EtOH (Table 1). In the case of PPOH, we suppose that a methyl group hinders the nucleophilic attack of HDI due to a steric effect, as can be seen in the activity and conversion results (Table1).

The proposed active species enables the discussion of the selectivity results. When a system produces exclusively diurethane, we may suppose that there is no elimination step of the monourethane precursor species after the initial attack of the alcohol to the NCO group of the coordinated HDI. For the system reported herein, which produces exclusively diurethane, ($Fe(acac)_3$ and $Cu(acac)_2$ with EPOH and PPOH; DBTDL with EPOH) complementary results of selectivity vs. time have shown no formation of monourethane product, even for low conversion conditions. These results corroborate that the monourethane precursor species remains in the coordination sphere of the active species when diurethane is produced exclusively. The monourethane precursor can then coordinate to the metal through its second free NCO group and a nucleophilic attack of the OH function leads then to diurethane.

In the case of the monourethane formed from EPOH and PPOH with the iron catalyst, the ester group which is present can coordinate with the iron via its carbonyl group, and the monourethane therefore remains in the coordination sphere of the metal (Scheme 1, **2**). A second nucleophilic attack can then occur which leads to the formation of diurethane. This kind of interaction has been described in the case of the methylacrylate dimerization catalyzed by Rh(III) complex [6,7]. As this kind of interaction does not exist when the alcohol is EtOH, the monourethane formed does not remain in the coordination sphere of the catalyst and, as the results show, monourethane is a reaction product. After this step, a competition between the coordination of a new HDI molecule and a monourethane molecule exists, leading to monourethane and diurethane, respectively (Table 1, S_D (%) = 52). Published studies pertaining to selectivity vs. time have shown that after 125 min when the conversion reaches 100%, diurethane is exclusively produced [2].

For the tin system, we observe that the selectivity depends on the nature of the alcohol. When the alcohol used is EPOH, only diurethane is produced. As we proposed for the iron catalyst, the precursor of the monourethane molecule remains in the coordination sphere of the active species through the interaction of the ester group (Scheme 1, **4**) leading then exclusively to the formation of diurethane. In the case of PPOH, steric hindrance due to the methyl group is detrimental to this interaction and monourethane is hence liberated. As HDI is more easily coordinated to the catalytic species compared to monourethane, for low conversion conditions, the conversion of HDI into monourethane is favored (Table 1, C (%) = 5 and S_D (%) = 0). Further studies show that the initial conversion of monourethane into diurethane is observed after 24 h. When EtOH is used, the absence of an ester group means that the monourethane precursor does not remain in the coordination sphere of the catalytic species and monourethane is then formed. Diurethane is also obtained because, for an equivalent reaction time (50 min), the conversion with EtOH is higher than with PPOH (32% and 5%, respectively). Monourethane is then in sufficient quantities to compete with HDI to be converted. Furthermore, published values of kinetic constants for the formation of monourethane ($k_M = 7 \cdot 10^{-3}$ min^{-1}) and diurethane ($k_D = 52 \cdot 10^{-3}$ min^{-1}) explain why diurethane is formed even for low HDI conversions. In this study, it has been also shown that diurethane selectivity increases up to 50% after 200 min of reaction time [2].

As for the copper catalyst, the exclusive formation of diurethane obtained when PPOH or EPOH are used, in a contrary manner to when EtOH is employed, is explained by the presence of the ester group in the case of PPOH and EPOH. Similar comments already made about the $Fe(acac)_3$ catalyst mechanism are also valid for the copper catalyst. The ester group interacts with the metal species, which leads to the monourethane precursor remaining the coordination sphere (Scheme 1, **6**), thus permitting a second nucleophilic attack and the formation of diurethane. Such an interaction does not exist when EtOH is used, resulting in the exclusive formation of monourethane, as shown by the selectivity results of Table 1.

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