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Investigations in the catalytic species of the distannoxane-catalyzed transcarbamoylation

B. Jousseaume,[a,]* C. Laporte,[a] T. Toupance[a] and J. M. Bernard[b]

[a]*Laboratoire de Chimie Organique et Organométallique, UMR 5802 CNRS, Université Bordeaux 1, 351, Cours de la Libération, F-33405 Talence Cedex, France*

[b]*Centre de Recherche des Carrières, Rhodia, 85 avenue des Frères Perret, BP 62, 69192 Saint-Fons, France*

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Abstract—1,3-Dihalodistannoxanes show a high activity as catalysts in transcarbamoylation, explained by the weak coordinative properties of the halogens, and act as Lewis acid and not alkoxide carriers in the catalytic cycle.

Ester interchange is a widely used reaction with important applications both for academic or industrial uses. It is an equilibrated reaction that can be shifted by the distillation of the volatile formed alcohol and thus allows the synthesis of esters under very mild conditions.[1] It is catalyzed by acids or bases and, among all possible catalysts, titanium alkoxides,[2] distannoxanes[3] and metal alkoxides[4] proved to be very efficient and useful. A particular case of ester interchange is transcarbamoylation where the alkoxide moiety of a carbamate is replaced by another one in the presence of an alcohol. This reaction is also catalyzed by acids or bases, metallic or organometallic derivatives being particularly helpful.[5] However, the reduced nucleophilic character of the carbamate carbonyl makes transcarbamoylation more difficult to perform than transesterification, allowing an elimination–addition mechanism to be contemplated, instead of, or in addition to a classical displacement mechanism.[6]

On the other hand, transcarbamoylation has important applications in polyurethane chemistry, especially for coatings.[7] Production of polyurethanes is usually achieved by addition of polymeric polyols on isocyanates. As this reaction is spontaneous at room temperature, mixing of the components just before use is essential. Moreover it is necessary to handle toxic isocyanates. To avoid these drawbacks, alternatives have been developed by the use of one-package systems. They involve blocked polyisocyanates and polyols, which do not react at room temperature, thus providing long pot lives. Under the influence of heating, a transcarbamoylation reaction occurs, leading to polyurethanes. For ease of application it is necessary to conduct the reaction at the lowest possible temperature, which can be achieved by using good leaving groups as blocking agent, methyl ethyl ketoxime for instance, and efficient catalysts.[8] However, to reduce toxic volatile organic compound emissions and costs, other blocking agents such as aliphatic alcohols, which show the inconvenience to necessitate high reaction temperatures, would be preferable. It must be noted that a rate constant increased by a factor of two, which is often not very important in academic preparative synthesis, can be crucial in industry as it corresponds to a gain of about 10°C for a similar reaction progress. To allow their use under reasonable conditions, more active catalysts are currently researched. Organotin compounds such as dialkyltin dicarboxylates proved to be as efficient in transcarbamoylation reactions as they are in transesterifications.[8] Recently it was disclosed that monoorganotin tricarboxylates are also good catalysts, the relative efficiency of mono- and diorganotin carboxylates depending on the nature of the polyol used.[9] The same authors also reported that polystannoxanes associated or not to a co-catalyst lower significantly the temperature of the transcarbamoylation reaction between oxime-blocked hexyl diisocyanate and acrylic polyols.[10] However no study has been driven on the influence of the nature of the heteroatomic group linked to tin and, while it is admitted that this electronegative group can be displaced during the transesterification reaction,[3a–e] the nature of the active species in the catalytic cycle has not yet been determined. In this paper are reported our investigations in this field.[11]

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* Corresponding author. Fax: +33-5-4000-6994; e-mail: b.jousseaume@lcoo.u-bordeaux1.fr

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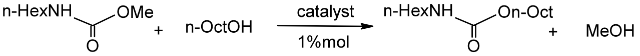
Otera showed that distannoxanes were the effective catalysts of transesterifications catalyzed by diorganotin compounds, the efficiency of the catalyst depending on the nature of the electronegative substituents of the tin, 1,3-dichloro- and 1-chloro-3-hydroxy-1,1,3,3-distannoxanes giving the best results at low concentration.[3a–e] In the present study, several distannoxanes have been prepared, used for the first time in a model transcarbamoylation reaction and their activity compared. Thus, a stoichiometric amount of *N*-hexyl *O*-methyl carbamate (3.14 mmol), 1-octanol (3.14 mmol), hexadecane as internal standard (1.57 mmol) and catalyst (1% mol) were heated at 122°C. A short path column allowed methanol to escape (Scheme 1).



Scheme 1. Transcarbamoylation reaction.

Aliquots of the reaction mixture were analyzed by GC to monitor the conversion of *N*-hexyl *O*-methyl carbamate in *N*-hexyl *O*-octyl carbamate. The reaction order in *N*-hexyl *O*-methyl carbamate was determined using a 10-fold excess of 1-octanol. An order of 1 was obtained by comparing the variation of concentration in carbamate with calculated curves for different values of order. The global order was determined by the same method from data obtained with identical concentration of the reactants. It was found equal to 2 which indicated a first order dependency on alcohol.

Results presented Table 1 indicate that symmetrical 1,3-ditriflyloxy-1,1,3,3-tetrabutyldistannoxane and unsymmetrically substituted 1-chloro-3-triflyloxy-1,1,3,3-tetrabutyldistannoxane show a lower activity than 1,3-diacetoxy-1,1,3,3-tetrabutyldistannoxane. Better results were obtained with distannoxanes symmetrically substituted by chloro or isothiocyanato groups but 1,3-dibromodistannoxane gave the highest rate of reaction, 1.3 time higher than with isothiocyanato substituents. With this catalyst, the yield of a reaction run for 3 h at 122°C was of 68% while it was of 89% in less than 2 h at 160°C, the reaction rate being 880×10^{-4} L mol^{-1} min^{-1}.

Table 1. Catalyzed transcarbamoylation of a *N*-alkyl *O*-alkyl carbamate

Catalyst	Rate constant[a]	Yield
ClBu$_2$SnOSnBu$_2$(OTf)[12]	6×10^{-4}	28[b]
((TfO)Bu$_2$Sn)$_2$O[12]	8×10^{-4}	28[b]
((AcO)Bu$_2$Sn)$_2$O[13]	14×10^{-4}	42[b]
(ClBu$_2$Sn)$_2$O[14]	18×10^{-4}	51[b]
((NCS)Bu$_2$Sn)$_2$O[15]	35×10^{-4}	62[b]
(BrBu$_2$Sn)$_2$O[14]	51×10^{-4}	68[b]
(BrBu$_2$Sn)$_2$O	880×10^{-4}	89[c]

[a] L mol^{-1} min^{-1}.

[b] % of *N*-hexyl *O*-octyl carbamate after 3 h at 122°C.

[c] % of *N*-hexyl *O*-octyl carbamate after 2 h at 160°C.

The mechanism generally admitted to explain the high catalytic activity of diastannoxanes in transesterifications consists in the displacement of an electronegative group linked to an external tin by a molecule of alcohol, which leads to an alkoxydistannoxane, the active catalytic species. It is followed by a nucleophilic attack of the alkoxide on the carbonyl of the ester, coordinated to a central tin of the dimeric distannoxane.[3a–e] To check if an alkoxydistannoxane was involved in the catalytic cycle of the transcarbamoylation, a reaction was conducted in the presence of 5% molar of 1,3-dichlorodistannoxane and followed by ^{119}Sn NMR. After 3 h at 122°C and about 50% completion, the NMR spectrum showed that the catalyst remained unchanged. In the same conditions, the less active 1,3-diacetoxydistannoxane was mainly transformed in mixed 1-acetoxy-3-alkoxydistannoxanes. After 3 h at 160°C, another acetoxyl ligand was replaced to give the corresponding dialkoxydistannoxane. So, two parallel processes seem to occur, catalysis and ligand exchange on tin. However, on the view of the results obtained with the 1,3-dichlorodistannoxane, which was recovered unchanged after the reaction and which is a more effective catalyst than the 1,3-dialkoxydistannoxane, the transfer of an alkoxide from tin to the carbamate in the catalytic cycle does not seem to be the most efficient way of catalysis. Analogous results were recorded recently in the distannoxane catalyzed transesterification either with fluorous[16] or conventionnal distannoxanes.[17]

As in the transesterification, the nature of the group linked to the tin has an important influence on the rate of the reaction. It is difficult to classify the activity of the catalysts according to the electronegativity of the substituents, which would make more acidic the tin centers and thus induce a more active electrophilic catalysis. In this case, triflate-substituted distannoxanes would give the higher rates. To rationalize our data, differences in steric effects and bonding should be taken in account. Transesterification is sensitive to steric effects on the ester group which is supposed to coordinate at the central tin of the distannoxane dimer.[18] Halides or straight isothiocyanates, less bulky than triflates or bridging carboxylates, should allow an easier access to the active central tin and thus enhance the activity of the corresponding distannoxane.

In conclusion, it has been demonstrated that 1,3-dibromodistannoxane has a very high activity in the organotin-catalyzed transcarbamoylation. Kinetic and ^{119}Sn NMR studies showed also that the catalyst does not act best as an alkoxide carrier but as a Lewis acid.

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