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MECHANISTIC INVESTIGATION OF DISTANNOXANE-CATALYZED URETHANE FORMATION STUDIED BY ^{119}Sn NMR SPECTRA[1)]

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The mechanism of urethane formation catalyzed by tetraorganodistannoxanes was investigated. The ^{119}Sn NMR spectra and the model reaction between methanol and phenyl isocyanate revealed that the formation of the alkoxy distannoxanes is the initial step.

Organotin compounds have proved to be the most efficient catalyst for urethane formation.[2)] There have appeared a number of suggestions on the catalytic mechanism;[3)] that is, i) the complex formation of tin compounds with isocyanates and alcohols followed by the reaction of the complex with the other reagent or by the reaction between the complexed reagents, ii) the metal alkoxide formation followed by addition to the isocyanate to give the stannylcarbamate, iii) the intermediacy of the dibutyltin laurate cation, $[Bu_2Sn(OCOC_{11}H_{23})]^+$, and iv) the conversion of the tin-alcohol complex into the tin alkoxide anion such as $[Bu_2Sn(OAc)_2 \cdot OMe]^-$.

In 1967, Yokoo et al. have disclosed that some kinds of tetraorganodistannoxanes are 1000 times more active than organotin compounds usually employed so far such as dibutyltin dilaurate.[4)] It seems of great interest to elucidate the mechanism of this unusual catalytic activity in view of the distannoxane chemistry itself as well as the catalysis of organotin compounds.

Previously, we have revealed that distannoxanes in solution can be characterized to a considerable extent by means of ^{119}Sn NMR spectra.[5)] On this basis, the catalytic mechanism of distannoxanes has been investigated here by the use of the model system.

First of all, it is crucial to elucidate whether the catalyst reacts initially with the alcohol or the isocyanate. Addition of 10 equiv. of the alcohol to the $CDCl_3$ solution of $ClBu_2SnOSnBu_2OH$ (1) and $SCNBu_2SnOSnBu_2OH$ (2) at room temperature immediately induced lowfield shifts of ^{119}Sn NMR signals of distannoxanes. The results are summarized in Table 1 in which are listed $\delta(^{119}Sn)$ values of the corresponding alkoxides 3-5 that were prepared separately. Apparently, newly formed species are attributable to the alkoxides. The facile formation of alkoxides were confirmed by recrystallization of 1 and 2 from hot methanol. On the other hand, addition of phenyl isocyanate to the $CDCl_3$ solution of these distannoxanes gave rise to unidentifiable complex signals suggestive of decomposition of the distannoxane structure.

Table 1. Comparison of ^{119}Sn chemical shifts $\delta(^{119}Sn)$ of tetraorganodistannoxanes in the absence or presence of alcohols (10 equiv.) in $CDCl_3$ a)

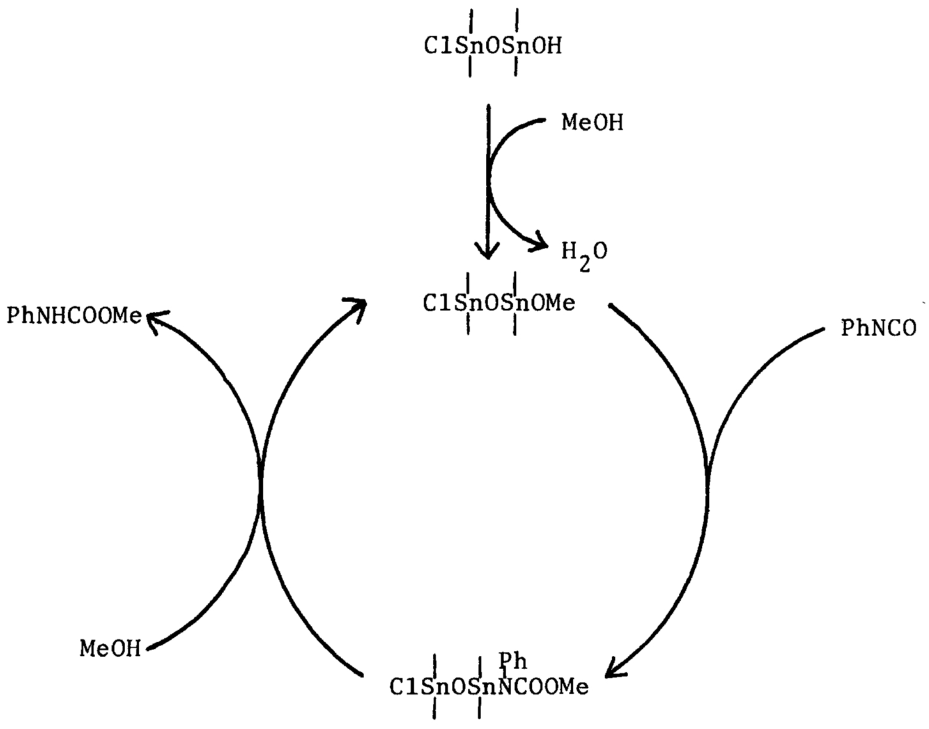
Distannoxane	Alcohol	δ/ppm b)
$ClBu_2SnOSnBu_2OH$ (1)	—	-158.6, -175.0
	MeOH	-155.0, -173.5
	$PhCH_2OH$	-150.3, -171.7
$SCNBu_2SnOSnBu_2OH$ (2)	—	-162.2, -211.8
	MeOH	-161.4, -208.5
$ClBu_2SnOSnBu_2OMe$ (3)	—	-155.4, -174.5
$ClBu_2SnOSnBu_2OCH_2Ph$ (4)	—	-151.2, -172.9
$SCNBu_2SnOSnBu_2OMe$ (5)	—	-161.4, -208.9

a) Conditions for ^{119}Sn NMR spectra measurements are described in Ref. 5.

b) Relative to internal tetramethyltin.

Next, the stoichiometric reaction of methanol and phenyl isocyanate was investigated in the presence of 1. Equimolar amounts of methanol and 1 were stirred in benzene at room temperature for 1 h. Addition of phenyl isocyanate to this mixture afforded methyl N-phenylcarbamate in 95% yield. By contrast, addition of methanol into the equimolar mixture of phenyl isocyanate and 1 which had been stirred in benzene at room temperature for overnight resulted in little formation of methyl N-phenylcarbamate. With no doubt, the above results indicate that the catalytic reaction is initiated by the formation of the methoxy distannoxane, which then adds to phenyl isocyanate as depicted in Scheme 1.6) This appears to be analogous to the mechanism proposed by Davies and his coworkers who suggested an alkoxide intermediate.7) Unfortunately, however, the intermediacy of an alkoxide species in the actual catalytic system has not necessarily been confirmed since their proposal is based on the reaction of trialkyltin alkoxides with isocyanates and so no explanation was put forth for the conversion of the organotin catalyst into the alkoxide.

Finally, the catalytic activity of phenoxy distannoxanes and methoxy- or phenoxytributyltin was compared in the reaction of phenyl isocyanate with *n*-butanol. Time-conversion curves are illustrated in Fig. 1,8) which clearly indicates a superior catalytic activity of distannoxanes. It is concluded therefore that the high catalytic activity of distannoxanes can be ascribed to the increased reaction rate of addition of phenyl isocyanate to the Sn-OR bond as well as the facile formation of the alkoxide.



Scheme 1.

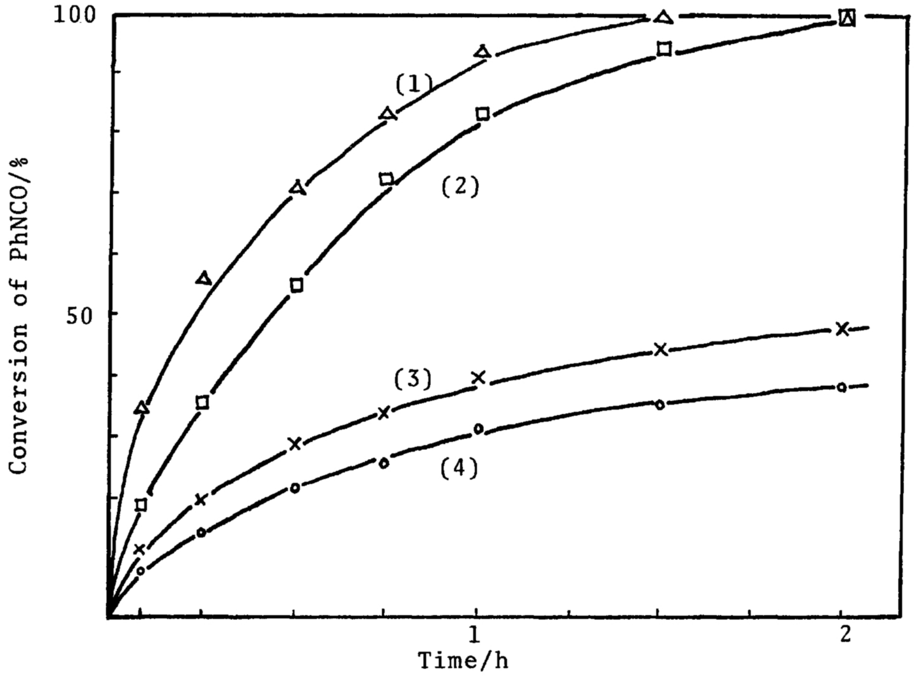
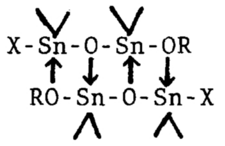


Fig. 1. Rate of organotin-catalyzed reaction between phenyl isocyanate and n-butanol at 30 °C: PhNCO/BuOH/cat./benzene = 10 mmol/10 mmol/5 x 10^{-4} mmol/30 ml. (1) $SCNBu_2SnOSnBu_2OPh$ (2) $ClBu_2SnOSnBu_2OPh$ (3) Bu_3SnOMe (4) Bu_3SnOPh.

Previously, we have suggested the oxygen-bridged dimerization of hydroxy or alkoxy distannoxanes which possess the rigid Sn-O-Sn-OR ring,5) so that the OH group in these compounds should be highly acidic. This seems why the hydroxy group in distannoxanes show such a unique reactivity. Of course, this structural feature may be responsible for acceleration of the addition of the alkoxy distannoxane to isocyanates since the bridged Sn-OR bond becomes more labile.



R = H, Me, Ph

X = Cl, Br, NCS

In summary, it is now revealed that the distannoxane-catalyzed urethane formation proceeds via the alkoxy intermediate and the role played by the oxygen-bridged dimeric structure is of prime importance. To the best of our knowledge, this is the first example that could have sorted out the explicit intermediate in tin-catalyzed alcohol-isocyanate reactions.

References

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