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Utility of Lewis Bases in Alkyltin Trithiolate Stabilizer Systems for Poly(vinyl chloride)

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ABSTRACT: Three monodentate ligands (pyridine *N*-oxide, tetrahydro-2*H*-thiopyran 1-oxide, and tetrahydro-1,3-dimethyl-2(1*H*)-pyrimidinone) are evaluated as potential components of monoalkyltin-based stabilizer systems for poly(vinyl chloride) (PVC). All of the ligands (L) form complexes of stoichiometry $RSnCl_3 \cdot L_2$ with alkyltin trichlorides and act as inhibitors of the alkyltin trichloride catalyzed dehydrochlorination of the allylic chloride *trans*-6-chloro-4-decene. The effectiveness of the ligands as inhibitors correlates with their affinities for the trichlorotin compounds, as determined by ^1H NMR measurements. Furthermore, methylthiolation of the allylic chloride by $CH_3Sn(SCH_3)_3$ proceeds even in the presence of excess ligand. These results suggest that suitable basic complexing agents can be used to mitigate the degradation of PVC by alkyltin trichlorides that are formed in the polymer and that it should be possible to devise improved PVC stabilizer systems containing an alkyltin trithiolate and a Lewis base.

It has been recognized for some time that monoalkyltin(IV) thiolates are exceptionally good color stabilizers for poly(vinyl chloride) (PVC) during the early stages of the thermal degradation of the polymer.[1] In this respect these thiolates are superior to the dialkyltin(IV) thiolates[1a,c–e] that are used more often with PVC in commercial applications.[1a,2] A reasonable explanation for this superiority is that the monoalkyltins are more reactive than their dialkyltin counterparts in processes, such as reaction 1, that convert the thermally labile structures of the

$$\text{-CH=CH—CHCl-} \xrightarrow[R_2Sn(SR')_2]{RSn(SR')_3\text{ or}} \text{-CH=CH—CHSR}'\text{-} \quad (1)$$

R = alkyl

R′ = alkyl or substituted alkyl

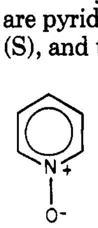
polymer (allylic and/or tertiary chloride)[3] into groups that are much more stable.[1d,e] Unfortunately, however, the long-term heat stability conferred by the monoalkyltins is significantly less than that produced by their dialkyltin analogues.[1b–d,4] Moreover, when the stabilizers are exhausted and the polymer begins to degrade significantly, it does so much more rapidly when the monoalkyltins are used.[1b–d]

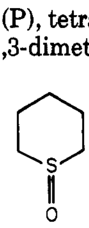
These inferior properties of the monoalkyltins can be explained by their conversion into monoalkyltin(IV) chlorides ($RSnCl_3$) during the stabilization induction periods.[1b,d] Such chlorides are stronger Lewis acids than the R_2SnCl_2 chlorides that are formed from the analogous dialkyltin(IV) thiolates,[5] and there is abundant evidence to show that they are far more effective than the latter chlorides as catalysts for the dehydrochlorination of the polymer.[1b,6] In addition, a model-compound study has suggested that, not surprisingly, they also are the more effective type of catalyst for reactions of organotin(IV) stabilizers with the ordinary monomer units of PVC.[4] Such reactions are, of course, undesirable, for they simply consume the stabilizer without providing any useful effects in return.

In view of these considerations, it would seem that the stabilizing properties of monoalkyltin(IV) thiolates could be improved considerably if the deleterious consequences of $RSnCl_3$ formation could be avoided in some way. One approach to this problem is to transform the chlorides back into their thiolate progenitors in situ, and a recent study[6b] has suggested that such a conversion may be responsible (in part, at least) for the well-known synergistic phenomena that are observed when mixtures of monoalkyl- and dialkyltin(IV) thiolates are used to stabilize PVC.[1a–c,e,2b,6b,d] Another approach would simply be to deactivate the chlorides as soon as they are formed by converting them into stable coordination complexes in reactions with Lewis bases. Very few efforts along this line have been reported, although van Hoang et al.[6a] have shown that tributylphosphine and pyridine are able to retard the $BuSnCl_3$-catalyzed dehydrochlorination of a mixture of allylic chlorohexenes at 60 °C. However, these Lewis bases may not be useful with PVC itself, since trioctylphosphine[7] and pyridine[8] are known to cause the rapid dehydrochlorination of the polymer when processing temperatures are reached.

In order to function most effectively in the polymer system, a complexing agent needs to fulfill the following chemical requirements: (a) It must quickly convert the $RSnCl_3$ into a complex that is very stable and noncatalytic. (b) It must not stimulate the dehydrochlorination (or other undesirable reactions) of the polymer.[9] (c) It must not complex appreciably with the stabilizer itself or otherwise interfere significantly with the chemistry that imparts stability. Some interference may well occur, even under the best of conditions, since the $RSnCl_3$'s are likely to be able to catalyze desirable reactions such as that of eq 1. On the other hand, this catalysis is probably not necessary for effective stabilization, in which case its absence would be inconsequential. In addition, some complexing agents for $RSnCl_3$ might also complex to lesser degrees with $RSn(SR')_2Cl$ and $RSn(SR')Cl_2$ intermediates, which can be presumed to have stabilizing properties. One would hope to be able to minimize or avoid this difficulty by using complexing agents that are highly selective.

This paper describes an investigation of three weakly basic monodentate ligands as potential components of monoalkyltin-based PVC stabilizer systems. These ligands are pyridine *N*-oxide (P), tetrahydro-2*H*-thiopyran 1-oxide (S), and tetrahydro-1,3-dimethyl-2(1*H*)-pyrimidinone (U).


P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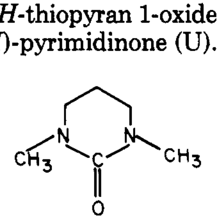
U

This series was chosen because all three bases are fairly rigid and nearly isosteric. Therefore, differences in their behavior may be attributed mainly to their functionalities. Groups of similar structure would also be candidates for

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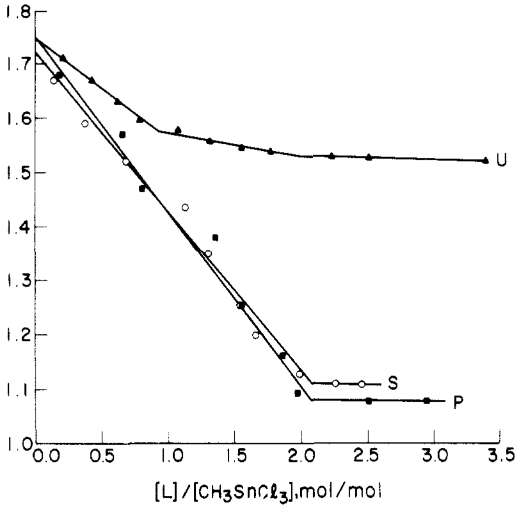

Figure 1. Methyl proton NMR chemical shifts for CH_3SnCl_3 as a function of the number of equivalents of added ligand in CD_3CN.

incorporation into rigid multidentate ligands which might be more effective inhibitors of tin-mediated PVC degradation than the monodentate ligands discussed herein.

Experimental Section

All solvents were reagent grade. Pyridine *N*-oxide was dried by boiling out water as a benzene azeotrope, precipitating with hexane, and removing solvent under vacuum. Ligand S was prepared by the oxidation of pentamethylene sulfide with $NaIO_4$;[10] the absence of sulfone from the product was verified by IR. The cyclic urea U (Aldrich) was used without further purification, as were CH_3SnCl_3 (Alfa) and $C_4H_9SnCl_3$ (Alfa). Solid CH_3SnCl_3 was handled in a nitrogen-filled glovebag. The preparations of $CH_3Sn(SCH_3)_3$ (from CH_3SnCl_3)[11] and *trans*-6-chloro-4-decene[12] are reported elsewhere. Nuclear magnetic resonance spectra were recorded on a JEOL FX90Q FT spectrometer containing a variable-temperature probe, using tetramethylsilane as an internal standard. Samples for NMR analysis of allylic chloride reactivity were prepared by weighing ligands (if any) directly into NMR tubes and adding aliquots of stock solutions of tin compounds and/or allylic chloride. Complexes $CH_3SnCl_3{\cdot}P_2$, $CH_3SnCl_3{\cdot}S_2$, and $CH_3SnCl_3{\cdot}U_2$ were crystallized from mixtures of dichloromethane and hexane and were dried at 110 °C under vacuum. All three complexes gave correct (± 0.3%) analyses (performed by Galbraith Laboratories, Inc., Knoxville, TN) for all elements that were present.

Results

Complexation of Methyltin Compounds by P, S, and U. Solutions of 0.5 g of CH_3SnCl_3 in 20 mL of dichloromethane containing 2 equiv of a ligand L (L = P, S, or U) deposited crystals of $CH_3SnCl_3{\cdot}L_2$ when treated with hexane and evaporated to the cloud point. The compositions of the crystalline complexes were verified by ^1H NMR and elemental analysis.

Aliquots of 0.16 M solutions of a ligand in CD_3CN, when added to 0.5 mL of 0.11 M CH_3SnCl_3 in CD_3CN, caused upfield shifts in the CH_3Sn proton magnetic resonance signal. Plots of this chemical shift vs. ligand/CH_3SnCl_3 mole ratio exhibited points of inflection at mole ratio 2 (Figure 1) in the cases of ligands P, S, and U. The data for ligand U revealed an inflection at mole ratio 1, as well. Spectra recorded at mole ratio 2 agreed with those of crystalline $CH_3SnCl_3{\cdot}L_2$ complexes dissolved in CD_3CN.

Competition experiments were performed by adding 2 equiv of each of two ligands to 0.032 mmol of CH_3SnCl_3 dissolved in ca. 1 mL of CD_3CN. The observed chemical shifts of the ligands were compared to measured values for totally free and totally tin-bound P, S, and U (Table I). The data served to establish the relative affinities of the ligands for CH_3SnCl_3 as P > S > U.

Table I
Proton Chemical Shifts (ppm vs. Me_4Si) for Ligands P, S, and U Dissolved in 0.03 M CH_3SnCl_3 in CD_3CN[a]

ligands in solution	δP[b]	δS[c]	δU[d]
P and S	8.57	2.88	
S and U		2.97	2.83
P and U	8.57		2.81
P or S or U, singly[e]	8.59	3.01	2.93
P or S or U, singly, no CH_3SnCl_3[f]	8.10	2.70	2.80

[a] Each ligand, when present, is at 0.06 M concentration. [b] Tallest peak of the 2- and 6-hydrogen multiplet. [c] Center of the 2- and 6-hydrogen multiplet. [d] Methyl proton singlet. [e] Chemical shifts of totally complexed ligands. [f] Chemical shifts of totally uncomplexed ligands.

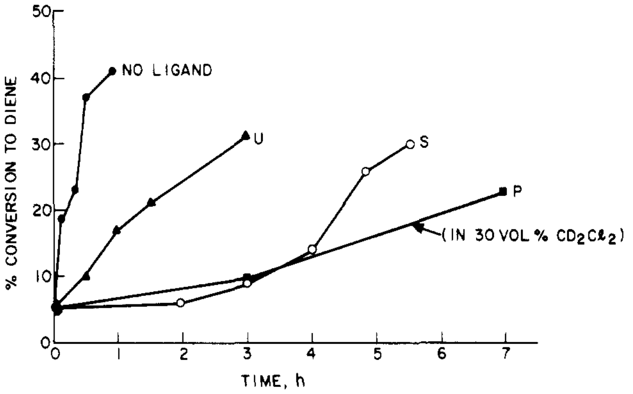

Figure 2. Dehydrochlorination of *trans*-6-chloro-4-decene [0.5 M in 15:85 (v/v) CD_2Cl_2–C_6D_6] catalyzed by 0.1 M butyltin trichloride in the presence of 2.1 equiv of added ligand. The percent conversion to diene is based on the integrated intensities of the methine and vinyl proton NMR signals.

The ^1H NMR spectrum of the model PVC stabilizer, $CH_3Sn(SCH_3)_3$ (0.05 M in CD_3CN), was unperturbed by the addition of 2 equiv of S or U. However, S and U did interact with a rapidly equilibrating[13] CD_3CN solution of CH_3SnCl_3 and $CH_3Sn(SCH_3)_3$. An intractable precipitate was formed on mixing $CH_3Sn(SCH_3)_3$ with P in CD_3CN.

Reaction of Alkyltin Compounds with an Allylic Chloride. When a solution of *trans*-6-chloro-4-decene (0.5 M) and methyl- or butyltin trichloride (0.1 M) in 15:85 (v/v) CD_2Cl_2–C_6D_6 was heated at 70 °C in an NMR tube, dehydrochlorination was initiated within minutes, as indicated by the decreased intensity of the allylic chloromethine proton NMR signal at 4.2 ppm, accompanied by the appearance of new signals at 6.0–6.5 ppm that were suggestive of conjugated dienes. Peaks attributable to allylbenzene moieties were not observed. The reaction mixture blackened when heated at 70 °C overnight.

The breakdown of the allylic chloride under these conditions was inhibited by the presence of 2.1 equiv of P, S, or U for each equivalent of tin compound. This inhibition is illustrated for the $C_4H_9SnCl_3$ case in Figure 2. Experiments with CH_3SnCl_3 were complicated by the tendency of the $CH_3SnCl_3{\cdot}L_2$ complexes to precipitate from solution but, nevertheless, gave results that supported the butyltin data. In addition, ligands P and U prevented the overnight blackening of the solution that was observed in the ligand-free case.

Tin-free solutions of the allylic chloride, with or without the ligands, were stable under the experimental conditions. Methyltin trichloride degraded the olefin under argon as well as under atmospheric oxygen.

The substrate *trans*-6-chloro-4-decene, as a 0.5 M solution in 15–30 vol % CD_2Cl_2 in C_6D_6, was heated at 70 °C with 0.6 mol equiv of $CH_3Sn(SCH_3)_3$. In the absence of additional ligands, complete conversion to (methylthio)decenes[14] occurred in 3 h, as determined by ^1H and ^{13}C NMR and by mass spectroscopy. When 1.3 equiv of U was added, over 80% conversion was observed in 3 h; complete reaction was noted in 6 h. The addition of S or P caused partial precipitation of the tin compound; nevertheless, the methylthiolation was completed in 24 h in the presence of an excess of these two ligands. No diene formation was noted by NMR during any of these methylthiolation processes.

Discussion

The formation of hexacoordinate complexes between alkyltin trihalides and Lewis bases is well documented.[15] The present investigation apparently introduces tetrahydro-2*H*-thiopyran 1-oxide and tetrahydro-1,3-dimethyl-2(1*H*)-pyrimidinone as new ligands for alkyltin trichlorides, and it also demonstrates the high affinities that these ligands possess for such tin compounds in weakly coordinating media. The inflection points seen in Figure 1 indicate that mixtures of CH_3SnCl_3 and the ligands form complexes which remain highly associated in solution.[16] This complexation seems to be selective for tin chlorides over $CH_3Sn(SCH_3)_3$, suggesting that a PVC stabilizer system containing an alkyltin trithiolate and a Lewis base would react to form alkyltin chloride complexes and free alkyltin trithiolate in a medium containing "defective" PVC.

The unsaturated compound *trans*-6-chloro-4-decene may be considered to be a model for a PVC defect site.[3] Examined here are two reactions of this model that are relevant to the use of alkyltin trithiolates as stabilizers for PVC: (1) alkyltin trichloride catalyzed dehydrochlorination, which leads to catastrophic degradation[1b] in actual polymer samples, and (2) thiolation of allylic chloride by alkyltin trithiolate, which is believed to effect stabilization in polymer specimens.[1d,e,4,6b,d]

The dehydrochlorination experiments lead to conclusions that are in agreement with those of a previous study,[6a] namely, that alkyltin trichlorides do indeed greatly stimulate HCl elimination from allylic chloroalkenes and that this process is retarded by the addition of Lewis bases. The data plotted in Figure 2 show a direct correlation between the effectiveness of the base in preventing olefin decomposition and its affinity for the tin atom in solution: $P > S > U$ in both cases. Furthermore, it is possible that at long reaction times, some of the observed degradation is due to autocatalysis by HCl, which might not be present in a properly stabilized PVC sample.

The slight inhibition of methylthiolation by the urea ligand lends support to a substitution mechanism involving coordination of the chloride leaving group to tin, which was originally proposed by Frye et al.[17] for R_2SnY_2 compounds. No such support could be drawn from the sulfoxide or pyridine *N*-oxide experiments, owing to the inhomogeneity of the reaction mixtures. In any event, it seems that through the use of more soluble alkyltin trithiolates combined with a Lewis base, defect site stabilization of PVC via reaction 1 should be achievable while avoiding the degradative effects of the alkyltin trichloride byproducts. Indeed, preliminary experiments on alkyltin trithiolate stabilized PVC containing pyridine *N*-oxide and cyclic sulfoxide additives indicate that these additives are effective in retarding discoloration of the PVC at 121 °C.[18]

In summary, the behavior of three cyclic monodentate ligands as alkyltin trichloride complexing agents has been investigated. These ligands decreased the activity of alkyltin trichlorides as dehydrochlorination catalysts for an allylic chloride. Nevertheless, methylthiolation of the allylic chloride by $CH_3Sn(SCH_3)_3$ occurred even in the presence of two full equivalents of the ligands and was not accompanied by dehydrochlorination. Thus the type of system studied here does seem to satisfy the three criteria that were mentioned in the introductory section, leading to the postulation of PVC stabilizer formulations containing an alkyltin trithiolate and a Lewis base.

Acknowledgment. We thank Dr. S. L. Haynie for a generous gift of *trans*-6-chloro-4-decene.

Registry No. P, 694-59-7; S, 4988-34-5; U, 7226-23-5; PVC (homopolymer), 9002-86-2; CH_3SnCl_3, 993-16-8; $C_4H_9SnCl_3$, 1118-46-3; $CH_3Sn(SCH_3)_3$, 4848-74-2; *trans*-6-chloro-4-decene, 90147-08-3.

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