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Studies on the disproportionation of trichloromethyltin

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The rate of disproportionation of trichloromethyltin in various solvents was studied by two methods, derivatization with sodium tetraethylborate and ^{13}C NMR measurements, which gave similar results. The reaction followed second-order kinetics and was more rapid in coordinating solvents than in uncoordinating ones. Moreover, it was catalyzed by nucleophiles, such as amines or alcohols, which is in favor of a nucleophile-assisted electrophilic reaction. Copyright © 2003 John Wiley & Sons, Ltd.

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INTRODUCTION

Organotin compounds occupy an important place in academic research, as well as in industrial chemistry. In organic synthesis[1] they are mainly used as reagents in reduction, transmetallation and coupling reactions, where the specific properties of hydrogen–tin and carbon–tin bonds fit particularly well with those of carbon–halogen, carbon–oxygen or carbon–metal bonds. The generally high selectivity of organotin reagents allows one to save time and to avoid product losses of protection–deprotection cycles. In industry, organotin[2] compounds are utilized for esterification and transesterification reactions, for silicone curing, for the preparation of polyurethanes, but the stabilization of poly(vinyl chloride) (PVC) is their largest application so far. PVC is one of the most versatile and cheapest of polymers used worldwide and is used in a wide variety of products, but it is unstable and may be degraded at processing temperatures. Stabilizers have to be added, often with a dual function against heat as well as slow light-degradation. Organotin compounds are very efficient for both purposes, since they are able to substitute the structural defects by more stable groups, to stop the dehydrochlorination by substituting an allylic chloride formed during thermal or light-induced degradation and to scavenge the hydrogen chloride evolved that would otherwise accelerate the decomposition process.[3] Methyl-, butyl- and octyl-tins are used with an equal success while the other groups linked to the metal are sulfur ligands. For efficiency reasons, mixtures of mono- and di-organotins are often recommended, monoorganotins being more efficient at inhibiting short-term degradation processes, whereas diorganotins are involved in mitigating long-term degradation processes. These stabilizers are obtained from the corresponding organotin halides, which are usually considered as stable compounds under their conditions of preparation and storage. This stability is important, as the toxicity of organotin compounds increases in going from mono- to di-, to tri- and tetraorganotins. Theoretically, a di-organotin cannot spontaneously convert into a triorganotin. This redistribution needs either another reactant or a catalyst.[4] However, it was reported some time ago that some scrambling of organic groups of organotin halides could occur at high temperature, the reaction being more rapid with a methyl group than with an ethyl group.[5,6] Because of the possible emergence of new regulations about the accuracy of the composition of organotin compounds, it was of interest to determine to what extent this scrambling reaction could occur at lower temperature in various solvents in the case of organotin trichlorides, which are important intermediates in the synthesis of PVC stabilizers.

RESULTS AND DISCUSSION

Grant and Van Wazer[7] reported on the redistribution reaction between tetramethyltin and tin tetrachloride, at 175 °C, with or without solvent:

$$Me_4Sn + SnCl_4 \longrightarrow Me_3SnCl + Me_2SnCl_2 + MeSnCl_3 \quad (1)$$

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The equilibrium constant of reaction (1) was deduced from the percentages of all the tin species present in the mixtures of tetramethyl-, chlorotrimethyl-, dichlorodimethyl-, trichloromethyl- and tetrachlorotin obtained using various tetramethyltin/tetrachlorotin ratios. It was found equal to 7×10^{-2}, which means that, when heated at 175 °C for a few days, trichloromethyltin partially redistributes to give a mixture of 17.5% of dichlorodimethyltin, 17.5% of tetrachlorotin and 65% of trichloromethyltin. In the case of ethyltin derivatives, the equilibrium of this reaction lies almost entirely on the left-hand side, as an equilibrium constant of 4×10^{-6} at 70 °C was found. We thus focused our study on methyltin compounds, which, from the above data, should give results able to be analyzed after reasonable delays. So, disproportionations of trichloromethyltin, obtained with a high purity from tricyclohexylmethyltin and tin tetrachloride,[8] were carried out by heating (50 °C) concentrated solutions (~2.9 M) of pure trichloromethyltin in various solvents to get significant formation of the products after a few days. Methyltin chlorides were not analyzed by gas chromatography (GC) directly from the reaction mixture, as some reactions between reactants and products could occur during the analyses and thus alter the results. Analyses on derivatized products were preferred. Pentylation with pentylmagnesium chloride,[9] which has been used successfully in speciation studies, was discarded, as it implies an extraction step when the study is conducted in a solvent susceptible to react with Grignard reagents. We turned our attention towards ethylation with sodium tetraethylborate, which can be performed even in the presence of protic solvents, such as alcohols or water, and has the advantage of leading to stable tetraorganotins, whereas sodium borohydride gives less stable organotin hydrides.[10] As the ethylation yield depends on the pH of the solution and on the amount of sodium tetraethylborate used, the experimental conditions were first optimized. The yields were obtained from GC analyses using undecane as internal standard after determination of the response factors. Variation of the pH of the ethylation solution from 4 to 6 increased the recoveries of triethylmethyltin and diethyldimethyltin from 15% to 60% and 100% respectively, with the maximum reached at pH 5. Then, the amount of sodium tetraethylborate was varied from two to ten equivalents per chlorine atom of trichloromethyl- and dichlorodimethyltin. With the trichloride the recovery increased from 60% to 100%, and for the dichlorodimethyltin to 100%. Hence, in this study, we fixed ethyl/chlorine ratio at 5, where 100% recovery was obtained. To check the reliability of these results, an NMR study was conducted in parallel. ^{1}H NMR could not be used to perform quantitative analyses of trichloromethyltin–dichlorodimethyltin mixtures, as the methyl resonances occur at the same chemical shift in water. We turned to ^{13}C NMR, where it is easier to differenciate between the two species. Spin-lattice relaxation times were measured through the inversion recovery method. The T_1 of dichlorodimethyltin reached 9.3 s, whereas it was only 6.3 s for trichloromethyltin. NMR experiments were thus performed with a relaxation delay between pulses of five times the longer T_1, which corresponds to 50 s and lengthens the acquisition times to about 3 h.

Then the overall order of the reaction was determined, at 50 °C in water for various concentration values (2.9, 1.35 and 0.75 M). It was first checked that in these conditions trichloromethyltin did not undergo any hydrolysis, which is known to occur at low concentration.[11] However, ^{13}C NMR analysis showed that trichloromethyltin began to be noticeably hydrolyzed at 50 °C only at concentrations lower than 0.4 M, for which two new signals, corresponding to dichlorohydroxymethyl- and chlorodihydroxymethyltin, appeared at higher field than the resonance of trichloromethyltin.

$$\mathrm{MeSnCl_3\ (0.4\ M\ in\ H_2O)} \longrightarrow \mathrm{MeSnCl_2OH} + \mathrm{MeSnCl(OH)_2} \qquad (2)$$

Plotting the concentration of trichloromethyltin versus time gave a good correlation for second-order kinetics, whatever the concentration, in agreement with what was determined earlier for the reaction of methyltriorganotins with methyltin halides or nitrates in alcohols as the solvent.[12] The values of 2.5×10^{-7} l mol^{-1} s^{-1} calculated from GC analysis data agreed reasonably well with the value of 3.3×10^{-7} l mol^{-1} s^{-1} calculated from NMR data. Hence, from hereon, we use the mean values of the data obtained from both methods. So, 26% of trichloromethyltin was transformed into dichlorodimethyltin and tetrachlorotin, after 96 h at 50 °C.

$$2\mathrm{MeSnCl_3} \longrightarrow \mathrm{SnCl_4} + \mathrm{Me_2SnCl_2} \qquad (3)$$

Addition of 0.66 equivalents of sodium hydroxide partially hydrolyzed trichloromethyltin[13] without inducing any precipitation, which started when one equivalent was added. The rate of disproportionation was similar to that of the pure compound (2×10^{-7} l mol^{-1} s^{-1}).

It has been reported that the addition of sodium chloride to a solution of tetramethyltin and dichloromethyltin decreases the rate of the electrophilic cleavage of methyl groups by a factor of nine.[12] In our case, the opposite effect was observed, as an increase of the rate by a factor of four was recorded ($k = 1.2 \times 10^{-6}$ l mol^{-1} s^{-1}). The addition of sodium perchlorate had a similar effect, but to a lower extent ($k = 8 \times 10^{-7}$ l mol^{-1} s^{-1}).

In order to broaden the scope of this study, water was substituted with other solvents at concentrations ranging from 2.85 to 3 M at 50 °C. A rapid decrease of the disproportionation reaction rate was observed when going from the more polar 2-propanol to the less polar toluene. The rate constant of 1.8×10^{-7} l mol^{-1} s^{-1} was measured for the reaction conducted in 2-propanol, not far from 2.9×10^{-7} l mol^{-1} s^{-1} recorded with water as solvent. In dibutyl ether and toluene, the rate constants were 5.5×10^{-9} l mol^{-1} s^{-1} and 1.4×10^{-9} l mol^{-1} s^{-1} respectively. At 50 °C in these solvents, significant changes of concentration of trichloromethyltin were on the order of tens of days (4% decrease after 28 days in toluene) not of hours, like when the reaction was performed in water.

The effect of nucleophiles was investigated in nonpolar solvents like toluene. Various amounts of 2-propanol and dibutylamine were added to a concentrated solution of trichloromethyltin in toluene. The presence of 5% of 2-propanol did not change the rate constant. However, at 10% of 2-propanol the rate constant almost tripled, reaching 4×10^{-9} l mol^{-1} s^{-1}, and with 10% of dibutylamine the effect was even stronger (1×10^{-7} l mol^{-1} s^{-1}).

From these data it is clear that nucleophilic activation is the key step of the disproportionation reaction of trichloromethyltin, as shown by the effect of solvent, the salt effect observed in water and the last results obtained in the presence of catalytic amounts of amine. The complexation of the tin by the nucleophile enhances its coordination and lengthens the tin–methyl bond, which becomes more susceptible to cleavage by the tin–chlorine bond of another molecule. In water, the water molecules act both as a strong nucleophile and a highly polar solvent, which enhances the rate of the disproportionation reaction, the driving force being the higher solvation energy of dichlorodimethyltin and tetrachlorotin than that of trichloromethyltin. Such a redistribution has recently been described in organosilicon chemistry. When trichlorosilane was treated with *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (teeda), silicon tetrachloride and a novel six-coordinate complex, (teeda)SiH_2Cl_2, were isolated.[14] The same reaction occurred with an analogous tridentate ligand.[15,16] Thus, in the presence of a strong ligand, even a strong silicon–hydrogen bond can be cleaved, leading to disproportionation products.

In summary, we have studied the rate of disproportionation of trichloromethyltin in various solvents by two methods, derivatization with sodium tetraethylborate and ^{13}C NMR measurements. The reaction followed second-order kinetics and was more rapid in coordinating solvents than in uncoordinating ones. Moreover, it was catalyzed by nucleophiles, such as amines or alcohols, which is in favor of a nucleophile-assisted electrophilic reaction.

EXPERIMENTAL

All reactions were carried out under a nitrogen atmosphere. Pentane, diethyl ether, dibutyl ether and toluene were distilled from sodium benzophenone ketyl prior use. Dibutylamine was distilled over CaH_2. 2-Propanol was distilled over magnesium. Tin tetrachloride was distilled before use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer (solvent $CDCl_3$); ^{119}Sn NMR spectra were recorded on a Bruker DPX-200 spectrometer (solvent $CDCl_3$).

Methyltricyclohexyltin

In a three-necked flask under nitrogen, methylmagnesium iodide was prepared from methyl iodide (72.42 g, 510 mmol) and magnesium (12.24 g, 510 mmol) in 300 ml of dry diethyl ether. The mixture was then refluxed for 1 h and was added slowly to a suspension of tricyclohexyltin hydroxide (80 g, 208 mmol) in 150 ml of dry diethyl ether. The resulting mixture was refluxed overnight and was then hydrolyzed after cooling with a saturated solution of ammonium chloride. After drying and evaporation of the solvents, methyltricyclohexyltin was recovered after distillation under high vacuum as a colorless oil; $bp_{0.001} = 140\,°C$. Yield: 82%, 66.3 g.

^{1}H NMR δ: 0 (3H, s,$^{2}J_{SnH} = 44.3$ Hz); 1.2–2 (33H, m). ^{13}C NMR δ: −16; 27 ($J_{SnC} = 7.6$ Hz); 28.9 ($^{3}J_{SnC} = 64$ Hz); 31 ($^{2}J_{SnC} = 15$ Hz); 34.2 ($^{1}J_{SnC} = 318$ Hz).

Methyltin trichloride

In a 250 ml Schlenk flask under nitrogen a solution of tin tetrachloride (21.4 g, 81 mmol) in pentane was added, at 0 °C, to a solution of methyltricyclohexyltin in pentane (42 g, 110 mmol). The solution was stirred at room temperature overnight. The solvent was removed and methyltin trichloride was sublimed under vacuum at 50 °C. The ^{1}H NMR spectrum indicated a purity higher than 99%. Yield: 75%.

Reference ethylmethyltins

In a dry 100 ml Schlenk tube, the desired organotin halide and 20 ml of freshly distilled diethyl ether were introduced under a stream of nitrogen. At room temperature, a solution of ethylmagnesium in diethyl ether (1.5 equivalents per chlorine atom) was slowly added via a syringe. The mixture was stirred for 15 h at room temperature. The solution was hydrolyzed with a saturated aqueous solution of ammonium chloride. The organotin derivative was extracted three times with diethyl ether. The organic phase was dried over magnesium sulfate. Diethyl ether was eliminated under vacuum and the organotin compound was distilled under vacuum or at atmospheric pressure.

$SnEt_4$: $bp_{20} = 95\,°C$. ^{1}H NMR δ: 0.82 (8H, q, $^{3}J_{HH} = 8.2$ Hz); 1.14 (12H, t, $^{3}J_{HH} = 8.2$ Hz). ^{13}C NMR δ: −0.35 ($^{1}J_{SnC} = 320$ Hz); 11.03 ($^{2}J_{SnC} = 24$ Hz). ^{119}Sn NMR δ: 2.4.

$MeSnEt_3$: $bp_{20} = 90\,°C$. ^{1}H NMR δ: −0.05 (3H, s, $^{2}J_{SnH} = 39$ Hz); 0.76 (6H, q, $^{3}J_{HH} = 6.3$ Hz); 1.14 (9H, t, $^{3}J_{HH} = 6.3$ Hz). ^{13}C NMR δ: −14.52 ($^{1}J_{SnC} = 286$ Hz); 0.62 ($^{1}J_{SnC} = 336$ Hz); 10.83 ($^{2}J_{SnC} = 24$ Hz). ^{119}Sn δ: 7.

Me_2SnEt_2: $bp_{758} = 150\,°C$. ^{1}H NMR δ: −0.02 (6H, s, $^{2}J_{SnH} = 40$ Hz); 0.77 (4H, q, $^{3}J_{HH} = 6.4$ Hz); 1.13 (6H, t, $^{3}J_{HH} = 6.4$ Hz). ^{13}C NMR δ: −12.68 ($^{1}J_{SnC} = 301$ Hz); 1.65 ($^{1}J_{SnC} = 354$ Hz); 10.69 ($^{2}J_{SnC} = 24$ Hz). ^{119}Sn δ: 7.3.

Kinetic study

In a 25 ml Schlenk tube, $MeSnCl_3$ (50% by weight) and the solvent were introduced under nitrogen. The Schlenk tube was then placed into a thermostatic bath at 50 °C (±0.1 °C). At known intervals, 0.5 ml aliquots of solution were taken off for analysis.

Ethylation for GC analysis

Into a 50 ml Schlenk tube was placed 10 μl of solution. The solution was buffered to pH 4.96 with a solution of sodium acetate/acetic acid in water. 1 ml of a solution of undecane in petroleum ether ($C = 0.04$ M) and 2 ml of petroleum ether were added. Then 1.5 ml of a solution of sodium tetraethylborate in water (50 mg ml^{-1}) was added in two portions. The solution was stirred vigorously for 30 min. Then, 0.5 μl of organic phase was analyzed directly by GC.

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