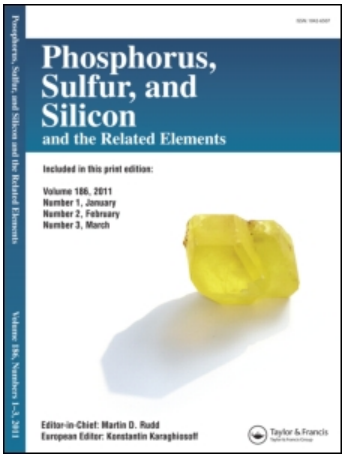


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# Equilibria in Organo Antimony Ring Chemistry

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# EQUILIBRIA IN ORGANO ANTIMONY RING CHEMISTRY

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Abstract. Reactions of ethyl antimony and n-propyl antimony rings give equilibria with the mixed substituted derivatives $R_{(n-m)}R'_mSb_n$ (n = 4, m = 1 - 3; n = 5, m = 1 - 4; R = Et, R'= n-Pr). The equilibrium constant K = $[(EtSb)_4]^5/[(EtSb)_5]^4$ has been determined as K = $9 \cdot 10^{-8}$ mol/l. Air oxidation of $p\text{-TolSb}(SiMe_3)_2$ gives yellow crystals of p-tolylantimony. In solution $(p\text{-TolSb})_5$ is the most abundant of p-tolyl antimony rings.



## INTRODUCTION

Organo antimony rings $(RSb)_n$ with bulky substituents (R = $tBu^1$, $Mes^2$, $(Me_3Si)_2CH^3$) are tetramers as crystals and preserve this ring size also in solution and in the gas phase due to kinetic stabilization. In contrast rings $(RSb)_n$ with sterically less demanding substituents (R = $Et^2$, $n\text{-}Pr^2$, $i\text{-}Pr^{3,4}$, $n\text{-}Bu^2$) form polymers in the solid state and tetramers or pentamers in benzene solution. In the mass spectra of unbranched alkyl antimony rings the most abundant species are

trimers. These results suggest that antimony rings with slim substituents are kinetically labile and take part in ring ring equilibria of pentamers and tetramers. There is however one six membered organo antimony ring, $(PhSb)_6$. This hexamer has been stabilized in the crystal. It is not known if phenyl antimony is kinetically stable and preserves the hexameric structure in solution mainly because $^1$H-NMR spectra are complex.
In this investigation we have concentrated on reactions of organo antimony rings with ethyl, n-propyl and p-tolyl (instead of phenyl) substituents and report here on ring ring equilibria in these systems.



## RESULTS

### Reactions of n-propyl antimony rings with ethyl antimony rings

The rings $(n\text{-}PrSb)_n$ (n = 4, 5) react with $(EtSb)_n$ (n = 4, 5) in benzene at room temperature in equilibria with formation of the mixed species according to Eq. (1).

$$(RSb)_n + (R'Sb)_n \rightleftharpoons R_{(n-m)}R'_mSb_n \qquad (1)$$

R = Et, R'= n-Pr, n = 4, m = 1 - 3; n = 5, m = 1 - 4

The novel ethyl propyl antimony rings have been detected both by NMR and mass spectroscopy. In the $^1$H NMR spectra of solutions of ethyl and propyl antimony rings in $C_6D_6$ new additional sharp multiplet signals appear immediately after mixing but they are too complex for a detailed analysis. The mixed rings are however easily detected in the mass spectra of concentrated solutions. Selected mass spectroscopic data are given in table I. The distribution of isotopes corresponds to theoretical values.

TABLE I Mass spectroscopic data of ethyl n-propyl antimony rings

| | | | |
|---|---|---|---|
| $Pr_4EtSb_5$ | $Pr_3Et_2Sb_5$ | $Pr_2Et_3Sb_5$ | $PrEt_4Sb_5$ |
| 810(1) | 796(1) | 782(2) | 788(1) |
| $Pr_3EtSb_4$ | $Pr_2Et_2Sb_4$ | $PrEt_3Sb_4$ | |
| 660(3) | 646(3) | 632(1) | |
| $Pr_2EtSb_3$ | $PrEt_2Sb_3$ | $Sb_3$ | |
| 480(25) | 466(10) | 365(100) | |

90 °C, 75 eV, m/z values, rel. intensities in ().

In the mass spectra of the mixed rings there are ions derived from trimers, tetramers and pentamers. Trimers or tetramers may be either fragments of the pentamers or molecular species present also in solution or formed on evaporation. As both ethyl and n-propyl antimony exist as tetramers and pentamers in solution we believe that this is also true for the mixed species.

Equilibrium between ethyl antimony rings

The distribution of ethyl antimony rings in benzene has originally been determined from the relative intensity of the NMR signals of a saturated solution as 88 % $(EtSb)_5$ and 12 % $(EtSb)_4$[2]. The tetramer/pentamer ratio is however not independent from the total concentration of ethyl antimony. Lower concentrations favour the tetramer in a reversible process. This is in agreement with the principle of le Chatelier and is explained by the equilibrium of Eq. (2).

$$4\ (EtSb)_5 \rightleftharpoons 5\ (EtSb)_4 \qquad (2)$$

In $C_6D_6$ at room temperature with 1,4-dioxane as internal standard the equilibrium constant $K = [(EtSb)_4]^5/[(EtSb)_5]^4$ has been determined as $K = 9\ 10^{-8}$ mol /l from the relative intensities of the $^1$H-NMR-signals of the tetramer and the pentamer.

p-Tolyl antimony.

The synthesis of p-tolyl antimony is very similar to the formation of $(PhSb)_6$. The various steps are described by the Eqs. (3) - (4).

$$p\text{-}TolSbCl_2 + Mg + 2Me_3SiCl \rightarrow p\text{-}TolSb(SiMe_3)_2 + MgCl_2 \quad (3)$$

$$p\text{-}TolSb(SiMe_3)_2 + 1/2\ O_2 \rightarrow 1/n\ (p\text{-}TolSb)_n + (Me_3Si)_2O \quad (4)$$

$p\text{-}TolSb(SiMe_3)_2$ is obtained in 62 % yield as a yellow oil that is self igniting on paper. The novel silyl stibane has been characterized by mass spectroscopy [70 eV, 20 °C; m/z (r. i. %) 358 (10)$M^+$, 149 (80), 73 (100)], elemental analysis and $^1$H-NMR spectra ($C_6D_6$; 0,38 s [18 H] $Me_3Si$, 2,10 s [3H] $CH_3$, 6,87 - 6,90 m; 7,57 - 7,60 m [4H] $C_6H_4$). The oxidation of $p\text{-}TolSb(SiMe_3)_2$ is best carried out in THF or toluene by a very slow access of air in the course of several days. Under these conditions p-tolyl antimony is formed in 26 % yield as yellow air stable crystals that analyze as $C_7H_7Sb$. The crystals formed are very small. The ring size of crystalline tolyl antimony therefore could not be determined by X ray crystallography. In the mass spectrum of the crystals the signal for the molecular ion of the pentamer $(pTolSb)_5$ [m/z = 1064 (1 %)] appears at highest mass. In addition signals of fragments of the pentamer as well as tetramers and trimers are also present. A selection

of mass spectroscopic data of p-tolyl antimony is given in table II.

TABLE II Mass spectroscopic data of p-tolyl antimony rings

| $p\text{-Tol}_5Sb_5$ | $p\text{-Tol}_4Sb_5$ | $p\text{-Tol}_4Sb_4$ | $p\text{-Tol}_3Sb_4$ |
|---|---|---|---|
| 1064(1) | 975(1) | 852(2) | 761(1) |

| $p\text{-Tol}_3Sb_3$ | $p\text{-TolSb}_3$ | p-TolSb |
|---|---|---|
| 638(50) | 456(5) | 212(100) |

90 °C, 75 eV, m/z values, rel. intensities in ().

The mass spectra confirm the identity of p-tolyl antimony as an antimony ring system but do not allow to determine the ring size in the condensed phase unambigiously. Additional informations come from the NMR spectra in the yellow benzene solution of carefully purified crystalline p-tolyl antimony in varying concentrations. The $^1$H-NMR spectral data are given in table III.

TABLE III $^1$H-NMR data of p-tolyl antimony at 360 MHz

$(p\text{-TolSb})_5$

$CH_3$ protons:δ, $C_6D_6$, 2.02 s [6 H], 2.06 s [6 H], 2.08 s [3 H], $CH_3$; $C_6H_4$ protons: 6.80 - 6.85 m [4 H], 6.88 - 6.91 m [4 H], 6.92 - 6.93 m [2H], 7.48 - 7.51 m [4H], 7.86 - 7.89 m [2H], 7.92 - 7.96 m [4H].

$(p\text{-TolSb})_4$ or $(p\text{-TolSb})_6$

$CH_3$ protons:δ, $C_6D_6$, 2.1 s [3H]; $C_6H_4$ protons: 6.9 - 6.95 m, 7.75 - 7.79 m [4 H].

The spectra show four singlet signals in the region of the methyl protons that fit in intensity to four pairs

of characteristic multiplet signals in the region of aromatic protons. This result is not compatible with the exclusive presence of $(p\text{-TolSb})_6$ but indicates the presence of rings of various sizes in solution. On dilution some signals preserve their intensity relative to each other while others do not. Thus the signal belonging to a specific ring are identified. The most intensive set of three signals has a 2:2:1 ratio that is typical for a pentamer where the substituents adopt a maximum of trans positions. We therefore associate these signals with the pentamer that was also detected in the mass spectrum. The remaining low intensity singlet signal in the methyl region and its counterparts in the aryl part of the spectrum indicate the presence of a ring with equivalent substituents, either the tetramer or the hexamer. In a saturated solution 88 % of the p-TolSb groups form $(p\text{-TolSb})_5$ and only 12 % are present in other rings. Similar distributions have also been found for alkyl antimony rings. The present results indicate that p-tolyl antimony belongs to the family of labile organo antimony rings in equilibria favouring pentamers.



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