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Preliminary communication

THERMAL DECOMPOSITION OF TETRAPHENYLANTIMONY MERCAPTIDES. EVIDENCE FOR A RADICAL ROUTE

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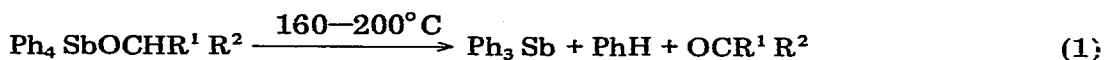
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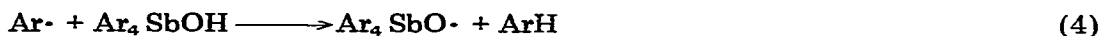
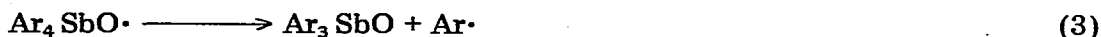
Summary

The thermal decomposition of $\text{Ph}_4\text{SbSC}_6\text{H}_4\text{X-}p$ occurs at least in part by a radical mechanism. Among the products are Ph_3Sb , $\text{PhSC}_6\text{H}_4\text{X-}p$ and $(p\text{-XC}_6\text{H}_4\text{S})_2$.

Certain tetraorganoantimony(V) compounds have been shown to be thermally unstable [1–3]. Thus heating alkoxy- and aroxy-tetraphenylantimony results in two decomposition reactions (eq. 1 and 2), while Me_4SbSR ($\text{R} = \text{Me}$, CH_2Ph and Ph) breaks down at room temperature to Me_3Sb and MeSR .



McEwen et al. have shown [3] that the thermal decomposition of Ar_4SbOH to Ar_3SbO and ArH proceeds via a free radical chain mechanism with the propagating steps as shown in eq. 3 and 4.

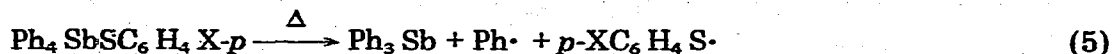


We now report that tetraphenylantimony mercaptides $\text{Ph}_4\text{SbSC}_6\text{H}_4\text{X-}p$ (I), are also thermally unstable and that at least part of the decomposition involves a radical route. Heating $\text{Ph}_4\text{SbSC}_6\text{H}_4\text{OMe-}p$ either in $\text{CHCl}_3/\text{CCl}_4$ or in PhH solutions in the presence of the spin trapping agent, $t\text{-BuNO}$, within the cavity of an ESR spectrometer, led to the detection of $t\text{-butyl phenyl nitroxide}$, $t\text{-Bu(Ph)NO}\cdot$ (II), an indication of the formation of phenyl radicals during the thermal decomposition. The ESR spectrum of II was identical to that obtained by Forrester and Calder [4].

The decompositions of I ($\text{X} = \text{OMe}$, Me and Br) proceed more readily than

that of Ph_4SbOPh (III), being complete within 2 h at 130°C in vacuo (compared to only 68% decomposition of III after 3 h at 200°C) or within 4 h in refluxing cyclohexane solution. Among the decomposition products of I are small amounts of PhH and Ph-Ph as well as Ph_3Sb , $p\text{-XC}_6\text{H}_4\text{SPh}$ (IV) and $(p\text{-XC}_6\text{H}_4\text{S})_2$ (V) in amounts dependent on X, e.g. yields of IV and V after complete decomposition of neat I were 40 and 55% respectively for $\text{X} = \text{OMe}$ and 94 and 2% respectively for $\text{X} = \text{Br}$.

The formation of $\text{Ph}\cdot$ from I we envisage occurring simultaneously with that of $p\text{-XC}_6\text{H}_4\text{S}\cdot$ (eq. 5) and that a chain mechanism does not apply. (Subsequent reactions will depend not only on X but also on the temperature and solvent.) The trapping of $p\text{-XC}_6\text{H}_4\text{S}\cdot$ as $t\text{-Bu}(p\text{-XC}_6\text{H}_4\text{S})\text{NO}\cdot$ and the latter's detection



is not possible at our reaction temperatures (between 50 to 80°C). Nitroxides, $\text{R}(\text{R}'\text{S})\text{NO}\cdot$, have only been detected at low temperatures [5,6] as a consequence of their thermal instability, e.g. the half-life [5] of $2,3,5,6\text{-Me}_4\text{C}_6\text{H}(\text{PhS})\text{NO}\cdot$ is only about 3 s at room temperature.

Further investigation of the extent of the radical components in the decomposition of tetraorganoantimony(V) compounds is underway.

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