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Preliminary communication

THERMAL DECOMPOSITION OF TETRAPHENYLANTIMONY MERCAPTIDES. EVIDENCE FOR A RADICAL ROUTE

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Summary

The thermal decomposition of $Ph_4SbSC_6H_4X$-*p* occurs at least in part by a radical mechanism. Among the products are Ph_3Sb, $PhSC_6H_4X$-*p* and $(p\text{-}XC_6H_4S)_2$.

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 (R = Me, CH_2Ph and Ph) breaks down at room temperature to Me_3Sb and MeSR.

$$Ph_4SbOCHR^1R^2 \xrightarrow{160\text{—}200^\circ C} Ph_3Sb + PhH + OCR^1R^2 \quad (1)$$

$$Ph_4SbOR \longrightarrow Ph_3Sb + PhOR \quad (2)$$

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.

$$Ar_4SbO\cdot \longrightarrow Ar_3SbO + Ar\cdot \quad (3)$$

$$Ar\cdot + Ar_4SbOH \longrightarrow Ar_4SbO\cdot + ArH \quad (4)$$

We now report that tetraphenylantimony mercaptides $Ph_4SbSC_6H_4X$-*p* (I), are also thermally unstable and that at least part of the decomposition involves a radical route. Heating $Ph_4SbSC_6H_4OMe$-*p* either in $CHCl_3/CCl_4$ or in PhH solutions in the presence of the spin trapping agent, t-BuNO, within the cavity of an ESR spectrometer, led to the detection of t-butyl phenyl nitroxide, t-Bu(Ph)NO· (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 (X = 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-XC_6H_4SPh (IV) and $(p\text{-}XC_6H_4S)_2$ (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 X = OMe and 94 and 2% respectively for X = Br.

The formation of Ph· from I we envisage occurring simultaneously with that of p-$XC_6H_4S\cdot$(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-$XC_6H_4S\cdot$ as t-Bu(p-XC_6H_4S)NO· and the latters' detection

$$Ph_4SbSC_6H_4X\text{-}p \xrightarrow{\Delta} Ph_3Sb + Ph\cdot + p\text{-}XC_6H_4S\cdot \qquad (5)$$

is not possible at our reaction temperatures (between 50 to 80° C). Nitroxides, R(R'S)NO·, 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-$Me_4C_6H(PhS)NO\cdot$ 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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