Radiation Induced Br-Transfer from Ethylbromide to Triethylsilane
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The radiolysis of deoxygenated triethylsilane (Et3SiH) was studied in the presence of various concentrations of ethylbromide (EtBr) as a function of the radiation dose. Chain reactions are leading to rather high yields of Br-containing final products, e.g. using 0.93 mol/dm3 EtBr we obtained: Gj(Et3SiBr) = 138, Gj(HBr) = 40, Gj(Br2) = 15 and Gj(Et3Si−SiEt3) = 6, in addition to small amounts of unidentified oligomers. Based on the knowledge from previous steady-state and pulse radiolysis studies of Et3SiH, a probable reaction mechanism is postulated to allow explanation of the present results.

Introduction

The chemistry of silanes, especially of organopolysilanes, where the backbone is a linear chain of silicon atoms, has recently attracted much interest. In order to better understand the reaction mechanism, halogenated silanes were used. In an earlier work by Ihlein et al. [1] several halogenated silanes in 2-methyltetrahydrofuran have been used for studies on the radiolysis induced formation of specific radicals at −196 °C under steady-state conditions. The observed absorption spectra were attributed to the corresponding radical anions and neutral species. The reactivity towards the free electrons (e−) is found to decrease with increasing number of methyl groups and to rise with growth of phenyl groups of the silanes. Lugovoi et al. [2] studied the radiation induced oxidation of ethyldichlorosilane, which results in the formation of chlorine-containing disiloxane. In addition to this a radical-chain process has been observed in the co-telomerization of ethylene and 1-hexene with ethyldichlorosilane [3, 4]. Pure triethylsilane (Et3SiH) has been a subject of rather extensive steady-state and pulse radiolysis investigations [5]. As a consequence of the radiolysis, 19 final products in deoxygenated as well as in N2O saturated triethylsilane have been found and their initial G-values (Gj) determined. The total transient absorption with λmax = 260 nm disappears with an apparent rate constant of k = 1.85·109 M−1s−1.

Finally, the observation of polysilane radical anions [6] and the effect of side chains studies by pulse radiolysis have been reported recently [7].

The aim of the present studies was to investigate the possibility of radiation induced transfer of a halogen atom from a halogenated organic compound, e.g. ethylbromide (EtBr), to triethylsilane (Et3SiH) in airfree media.

Experimental

The chemicals used were of p. A. purity (Merck, Darmstadt). Triethylsilane was further purified as previously described [5]. Prior to irradiation high purity argon was bubbled through the solutions in the irradiation vessels for about 1 h in order to remove oxygen. Solutions of various concentrations of EtBr in Et3SiH were irradiated as a function of radiation dose.

A “Gammacell 220” (Atomic Energy of Canada Ltd.) was used as 60Co γ-source. The dosimetry was performed by means of ferrous-copper dosimeter [8] under the same experimental conditions (dose rate: 41 Gy/min)++.

The analysis of the Et3SiH/EtBr system irradiated at various doses was performed by GC (“Carlo Erba

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Fractovap 2300°; porapax Q Se 30 10% CPS 80/100; temperature upto 250 °C). The product yields were determined by comparison with the concentration of standard samples. Some analyses were carried out by combined GC/MS (Varian-Aerograph and Varian MAT CH7A with data system)+++

Results

Various concentrations of EtBr (0.23, 0.50, 0.93, 1.30, 1.75 and 2.69 mol/dm³) in Et₃SiH were used. As a consequence of the radiolysis of the Et₃SiH/EtBr-system two Br-containing products (HBr and Et₃SiBr) in addition to hexaethylsilane (Et₃Si—SiEt₃), Br₂ and a mixture of unidentified oligomers were obtained. Fig. 1 illustrates the course of the EtBr decomposition (G₁ = 58) and the formation of Et₃SiBr (G₁ = 32.8) and HBr (G₁ = 19.3) as a function of dose.

It is to be noted that the yield of Et₃SiBr is nearly a mirror-image of the EtBr decrease. The rather high product yields indicate the occurrence of chain reactions. The shape of the curves, however, strongly changes with increasing EtBr concentration. Using 0.93 mol/dm³ EtBr, the yield of Et₃SiBr is strongly increased (G₁ = 138) and is proportional to the absorbed radiation dose. Also the yields of HBr (G₁ = 40) and the decomposition of EtBr (G₁ = 205) are increased (Fig. 2).

A further increase of the EtBr content in the deoxygenated Et₃SiH resulted in a decrease of the product yields as shown in Fig. 3. The radiation induced decomposition of EtBr is also reduced. Under these conditions a recombination of the radicals very likely takes place leading to reformation of the starting compounds. This effect became even more pronounced with further increase of the EtBr-concentration up to 2.68 mol/dm³, where G₁(HBr) = 10 and G₁(Et₃SiBr) = 30.

+++ The valuable help by Doz. Dr. Alexej Nikiforov is greatly appreciated.
For a better survey the $G_v$-values obtained from all experimental series are compiled in Table I. Obviously the highest $G_v$-values of the products are observed by using 1.3 mol/dm$^3$ EtBr in Et$_3$SiH.

Table I. Initial $G_v$-values ($G_v$) of EtBr consumption and products formed by radiolysis of Et$_3$SiH in the presence of various EtBr concentrations.

<table>
<thead>
<tr>
<th>EtBr (mol/dm$^3$)</th>
<th>Consump. Et$_3$SiBr</th>
<th>HBr</th>
<th>Br$_2$</th>
<th>Et$_3$Si$-$SiEt$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.23</td>
<td>58</td>
<td>32.8</td>
<td>19.3</td>
<td>5</td>
</tr>
<tr>
<td>0.50</td>
<td>90</td>
<td>50</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>0.93</td>
<td>205</td>
<td>138</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td>1.30</td>
<td>250</td>
<td>140</td>
<td>44</td>
<td>n. d.</td>
</tr>
<tr>
<td>1.75</td>
<td>143</td>
<td>96.5</td>
<td>27</td>
<td>25</td>
</tr>
<tr>
<td>2.68</td>
<td>85</td>
<td>34</td>
<td>12</td>
<td>20</td>
</tr>
</tbody>
</table>

### Discussion

The primary radiolysis products resulting from Et$_3$SiH and their $G_v$-values (given in brackets) are presented by the brutto reaction (1) [5]:

$$\text{Et}_3\text{SiH} \rightarrow \text{H}, e^- \cdot (\text{Et}_3\text{SiH}^-\cdot e^-), \text{H}_2$$

(3.60)

$\text{CH}_3, \text{C}_2\text{H}_5, \text{Et}, \text{Et}_3\text{Si}, (0.075) (3.60) (3.75)$

Et$_3$SiH, CH$_3$CH$_2$SiH(He)$_2$, (3.60) (0.27)

CH$_3$CH$_2$SiH(He)$_2$, CH$_2$SiH(He)$_2$ (0.17) (0.075)

The most important species in the present case are: e$^-$, (Et$_3$SiH$^-\cdot e^-)$, H, Et$_3$Si, Et, Et$_3$SiH. At lower EtBr concentrations in Et$_3$SiH the following reaction steps are very likely:

EtBr + e$^-$ $\rightarrow$ Et$^+$ + Br$^-$

(2)

Et$_3$Si$^+$ + e$^-$ $\rightarrow$ Et$^+$ + Br$^-$ + Et$_3$Si$^+$

(3)

Et$_3$Si$^+$ $\rightarrow$ Et$^+$ + Et$_3$SiH$^+$

(4)

Et$_3$Si$^+$ + HBr $\rightarrow$ Et$_3$Si + H$_2$ + Br$^-$

(5)

Et$_3$SiH + Br$^-$ $\rightarrow$ Et$_3$Si + HBr

(6)

EtBr + H $\rightarrow$ Et$^+$ + HBr

(7a)

Et$_3$SiH $\rightarrow$ Et$^+$ + Et$_3$SiBr

(8a)

Et$_3$Si$-$SiEt$_3$ $\rightarrow$ Et$^+$ + Et$_3$SiBr

(8b)

Et$_3$SiH + Br$^-$ $\rightarrow$ Et$_3$Si + HBr

(9a)

Et$_3$SiH $\rightarrow$ Et$_3$Si$^+$ + Et$_3$SiH$^+$

(9b)

Et$_3$Si$^+$ $\rightarrow$ Et$_3$SiH$^+$ + Et$_3$SiH

(10)

According to reactions (2), (3), (7a), (8a) and (9b) Et$^+$ radicals are formed, which can initiate a chain reaction, namely:

$$\text{Et}_3\text{SiH} + \text{Et}^+ \rightarrow \text{Et}_3\text{Si} + \text{C}_2\text{H}_6$$

(11)

The Et$_3$Si radicals thus produced, together with those formed by reactions (4) to (6) and (10) are consumed by reaction (8a) resulting in the main product, Et$_3$SiBr and again Et$^+$ radicals. A second chain process is started by the formation of Br species (see reactions (5) and (9a)). The Br transients are consumed by reaction (6), whereby HBr and Et$_3$Si transients are resulting. Reaction (7a) also contributes to the formation of HBr. Probably to a small extent the radical cations Et$_3$Si$^+$ can react with Br$^-$ by an electron transfer in competition to reaction (4).

$$\text{Et}_3\text{SiH}^+ + \text{Br}^- \rightarrow \text{Br} + \text{Et}_3\text{Si}^+ \rightarrow \text{Et}_3\text{Si} + \text{H}$$

(12)

In this case three reactive species can be formed (Br, H and Et$_3$Si), which are consumed as shown above.

With increasing EtBr concentration a direct radiolysis starts to play a role, namely:

$$\text{EtBr} \rightarrow \text{EtBr}^* \rightarrow \text{Et} + \text{Br}^-$$

(13a)

$$\text{Et}^+ + \text{Br}^- \rightarrow \text{Et}^3 + \text{Br}^-$$

(13b)

Et$^+$ and Br$^-$ transients are strongly contributing to an increase of the main product yields. The Et$^+$ transients can be scavenged in the bulk of the solution, e. g.:

$$\text{Et}^+ + \text{Et}_3\text{SiH} \rightarrow \text{EtH}^+ + \text{Et}_3\text{Si}$$

(14a)

$$\text{EtH}^+ + \text{e}^- \rightarrow \text{Et}^+ + \text{Et}_3\text{SiH}^-$$

(14b)

The possible fate of Br$^-$ is shown by reactions (5) and (12). Clearly, these processes explain the strong rise of the product yields presented in Fig. 2 compared to those in Fig. 1.

With further increase of the EtBr concentration, however, a decrease of the product yields is observed (Fig. 3 and Table I). This effect can be referred to back reactions initiated by the higher yield of the species resulting from reactions (13) to (15), which can lead to a reformation of the starting compounds, e. g.:

$$\text{Et}^+ + \text{Br}^- \rightarrow \text{HBr}$$

(16)

$$\text{Et}_3\text{Si} + \text{H} \rightarrow \text{Et}_3\text{SiH}$$

(17)

Finally, it might be mentioned, that besides the formation of various products [5] the Et$_3$Si radicals can also combine to give hexaethyldisilane as shown in Table I (see reaction (18)). By increasing the concentration of EtBr in Et$_3$SiH, the probability of Br...
atom combination to Br2 is raised (Table II, reaction (19)).

\[
\begin{align*}
2 \text{Et}_3\text{Si} & \rightarrow \text{Et}_3\text{Si} - \text{SiEt}_3 \quad \text{(18)} \\
2 \text{Br} & \rightarrow \text{Br}_2 \quad \text{(19)}
\end{align*}
\]

**Conclusion**

The radiation induced formation of Et3SiBr and HBr from Et3SiH using various concentrations of EtBr in absence of air was investigated as a function of radiation dose. The highest product yields, \(G_1(\text{Et}_3\text{SiBr}) = 140\) and \(G_1(\text{HBr}) = 44\), were achieved by using 1.30 mol/dm\(^3\) EtBr. Taking into consideration the knowledge obtained by previous steady-state and pulse radiolysis studies of Et3SiH [5], a probable reaction mechanism involving chain reaction steps is presented. The method can be used for production of Et3SiBr.

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