Radiation Induced Br-Transfer from Ethylbromide to Triethylsilane

Yu. M. Lugovoi* and N. Getoff**

Institute of Theoretical Chemistry and Radiation Chemistry, University of Vienna and
Ludwig Boltzmann Institute of Radiation Chemistry, both Währingerstraße 38,
A-1090 Wien, Austria

The radiolysis of deoxygenated triethylsilane (Et_3SiH) 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/dm^3 EtBr we obtained: $G_i(Et_3SiBr) = 138$, $G_i(HBr) = 40$, $G_i(Br_2) = 15$ and $G_i(Et_3Si-SiEt_3) = 6$, in addition to small amounts of unidentified oligomers. Based on the knowledge from previous steady-state and pulse radiolysis studies of Et_3SiH, 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 readiation 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_{aq}^-) 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 (Et_3SiH) 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 N_2O saturated Et_3SiH have been found and their initial G-values

$(G_i)^+$ determined. The total transient absorption with $\lambda_{max} = 260$ nm disappears with an apparent rate constant of $k = 1.85 \cdot 10^9$ $M^{-1}s^{-1}$.

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 (Et_3SiH) 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 Et_3SiH were irradiated as a function of radiation dose.

A "Gammacell 220" (Atomic Energy of Canada Ltd.) was used as ^{60}Co-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 Et_3SiH/EtBr system irradiated at various doses was performed by GC ("Carlo Erba

---

* On leave from Department of Chemical Technology, Mendeleev University, Miusskaja Pl. 9, Moscow, USSR.

** Author to whom correspondence should be addressed.

+ G_i = initial G-value represents the yield (number of molecules produced per 100 eV absorbed energy) of final products calculated from the tangent through the coordinate origin to the yield-dose curve.

++ 1 Gy = 100 rad = $6.24 \cdot 10^{15}$ eV/g sample.

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/dm^3) in Et$_3$SiH were used. As a consequence of the radiolysis of the Et$_3$SiH/EtBr-system two Br-containing products (HBr and Et$_3$SiBr) in addition to hexaethyldisilane (Et$_3$Si–SiEt$_3$), Br$_2$ and a mixture of unidentified oligomers were obtained. Fig. 1 illustrates the course of the EtBr decomposition (G$_i$ = 58) and the formation of Et$_3$SiBr (G$_i$ = 32.8) and HBr (G$_i$ = 19.3) as a function of dose.
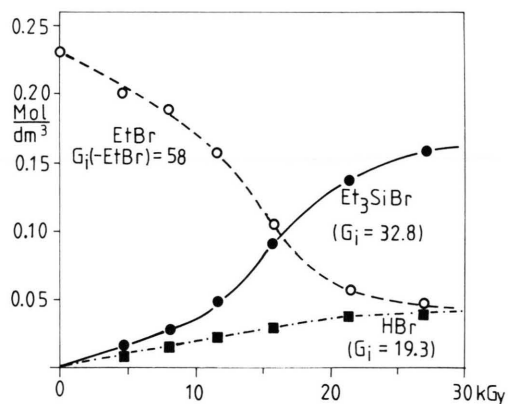
Fig. 1. Radiolysis of 0.23 mol/dm^3 ethylbromide (EtBr) in deoxygenated triethylsilane (Et$_3$SiH) with formation of Et$_3$SiBr and HBr as a function of dose.

It is to be noted that the yield of Et$_3$SiBr 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/dm^3 EtBr, the yield of Et$_3$SiBr is strongly increased (G$_i$ = 138) and is proportional to the absorbed radiation dose. Also the yields of HBr (G$_i$ = 40) and the decomposition of EtBr (G$_i$ = 205) are increased (Fig. 2).
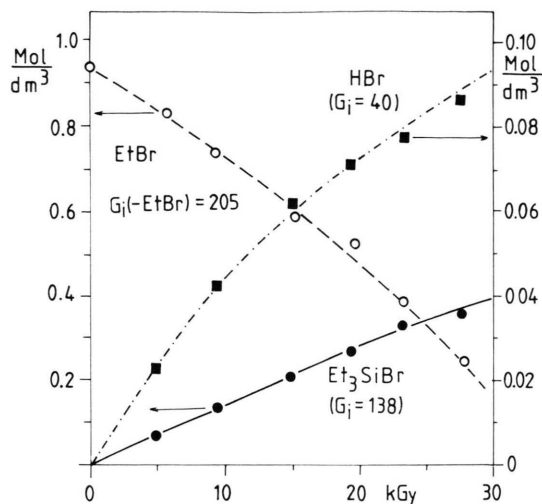
Fig. 2. Decomposition of EtBr as well as formation of Et$_3$SiBr and HBr from 0.93 mol/dm^3 EtBr in air-free Et$_3$SiH as a function of dose.

A further increase of the EtBr content in the deoxygenated Et$_3$SiH 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/dm^3, where G$_i$(HBr) = 10 and G$_i$(Et$_3$SiBr) = 30.
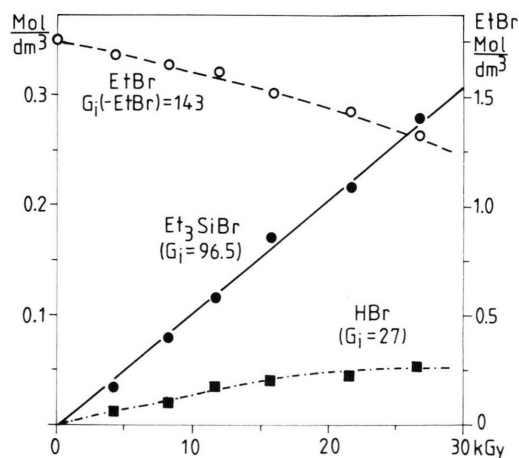
Fig. 3. Product formation (Et$_3$SiBr and HBr) and EtBr consumption by radiolysis of 1.75 mol/dm^3 EtBr in air-free Et$_3$SiH as a function of dose.
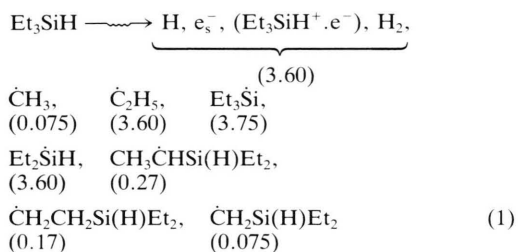
For a better survey the G_i-values obtained from all experimental series are compiled in Table I. Obviously the highest G_i-values of the products are observed by using 1.3 mol/dm³ EtBr in Et₃SiH.

Table I. Initial G-values (G_i) of EtBr consumption and products formed by radiolysis of Et₃SiH in the presence of various EtBr concentrations.
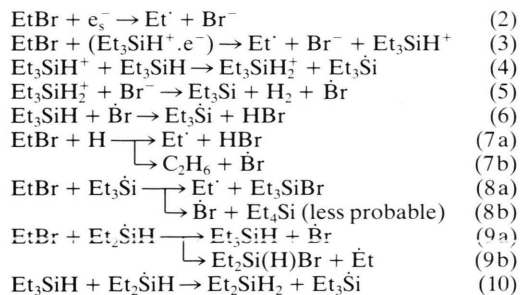
EtBr (mol/dm³) in Et₃SiH	G_i-values Consumpt. of EtBr	Et₃SiBr	HBr	Br₂	Et₃Si−SiEt₃
0.23	58	32.8	19.3	5	n.d.
0.50	90	50	20	8	8
0.93	205	138	40	15	6
1.30	250	140	44	n.d.	n.d.
1.75	143	96.5	27	25	n.d.
2.68	85	34	12	20	5

Discussion

The primary radiolysis products resulting from Et₃SiH and their G_i-values (given in brackets) are presented by the brutto reaction (1) [5]:

$$Et_3SiH \longrightarrow \underbrace{H, e_s^-, (Et_3SiH^+ \cdot e^-), H_2,}_{(3.60)}$$

$$\begin{array}{ccc} \dot{C}H_3, & \dot{C}_2H_5, & Et_3\dot{S}i, \\ (0.075) & (3.60) & (3.75) \end{array}$$

$$\begin{array}{cc} Et_2\dot{S}iH, & CH_3\dot{C}HSi(H)Et_2, \\ (3.60) & (0.27) \end{array}$$

$$\begin{array}{cc} \dot{C}H_2CH_2Si(H)Et_2, & \dot{C}H_2Si(H)Et_2 \\ (0.17) & (0.075) \end{array} \quad (1)$$

The most important species in the present case are: e_s^-, $(Et_3SiH^+ \cdot e^-)$, H, Et₃Si, Et, Et₂SiH. At lower EtBr concentrations in Et₃SiH the following reaction steps are very likely:

$$EtBr + e_s^- \rightarrow Et^{\cdot} + Br^- \quad (2)$$
$$EtBr + (Et_3SiH^+ \cdot e^-) \rightarrow Et^{\cdot} + Br^- + Et_3SiH^+ \quad (3)$$
$$Et_3SiH^+ + Et_3SiH \rightarrow Et_3SiH_2^+ + Et_3\dot{S}i \quad (4)$$
$$Et_3SiH_2^+ + Br^- \rightarrow Et_3Si + H_2 + \dot{B}r \quad (5)$$
$$Et_3SiH + \dot{B}r \rightarrow Et_3\dot{S}i + HBr \quad (6)$$
$$EtBr + H \begin{array}{l} \rightarrow Et^{\cdot} + HBr \quad (7a) \\ \rightarrow C_2H_6 + \dot{B}r \quad (7b) \end{array}$$
$$EtBr + Et_3\dot{S}i \begin{array}{l} \rightarrow Et^{\cdot} + Et_3SiBr \quad (8a) \\ \rightarrow \dot{B}r + Et_4Si \text{ (less probable)} \quad (8b) \end{array}$$
$$EtBr + Et_2\dot{S}iH \begin{array}{l} \rightarrow Et_3SiH + \dot{B}r \quad (9a) \\ \rightarrow Et_2Si(H)Br + \dot{E}t \quad (9b) \end{array}$$
$$Et_3SiH + Et_2\dot{S}iH \rightarrow Et_2SiH_2 + Et_3\dot{S}i \quad (10)$$

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

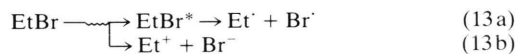$$Et_3SiH + Et^{\cdot} \rightarrow Et_3\dot{S}i + C_2H_6 \quad (11)$$

The Et₃Si radicals thus produced, together with those formed by reactions (4) to (6) and (10) are consumed by reaction (8a) resulting in the main product, Et₃SiBr 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 Et₃Si transients are resulting. Reaction (7a) also contributes to the formation of HBr. Probably to a small extent the radical cations Et₃SiH⁺ can react with Br⁻ by an electron transfer in competition to reaction (4).

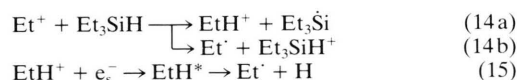$$Et_3SiH^+ + Br^- \rightarrow \dot{B}r + Et_3SiH^* \rightarrow Et_3\dot{S}i + H \quad (12)$$

In this case three reactive species can be formed (Br, H and Et₃Si), which are consumed as shown above.

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

$$EtBr \rightsquigarrow \begin{array}{l} EtBr^* \rightarrow Et^{\cdot} + Br^{\cdot} \quad (13a) \\ \rightarrow Et^+ + Br^- \quad (13b) \end{array}$$

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.:

$$Et^+ + Et_3SiH \begin{array}{l} \rightarrow EtH^+ + Et_3\dot{S}i \quad (14a) \\ \rightarrow Et^{\cdot} + Et_3SiH^+ \quad (14b) \end{array}$$
$$EtH^+ + e_s^- \rightarrow EtH^* \rightarrow Et^{\cdot} + H \quad (15)$$

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.:

$$Et^{\cdot} + Br^{\cdot} \rightarrow HBr \quad (16)$$
$$Et_3\dot{S}i + H \rightarrow EtSiH \quad (17)$$

Finally, it might be mentioned, that besides the formation of various products [5] the Et₃Si radicals can also combine to give hexaethyldisilane as shown in Table I (see reaction (18)). By increasing the concentration of EtBr in Et₃SiH, the probability of Br

atom combination to Br_2 is rised (Table II, reaction (19)).

$$2 Et_3Si \rightarrow Et_3Si-SiEt_3 \qquad (18)$$
$$2 Br \rightarrow Br_2 \qquad (19)$$

Conclusion

The radiation induced formation of Et_3SiBr and HBr from Et_3SiH using various concentrations of EtBr in absence of air was investigated as a function of radiation dose. The highest product yields, $G_i(Et_3SiBr) = 140$ and $G_i(HBr) = 44$, were achieved by using 1.30 mol/dm³ EtBr. Taking into considera-

tion the knowledge obtained by previous steady-state and pulse radiolysis studies of Et_3SiH [5], a probable reaction mechanism involving chain reaction steps is presented. The method can be used for production of Et_3SiBr.

[1] W. Ihlein, J. Wendenburg, and A. Henglein, Z. Naturforsch. **23b**, 1403 (1968).
[2] Yu. M. Lugovoi, A. G. Shostenko, N. P. Tarasova, C. Filliatre, and G. Bourgeois, React. Kinet. Catal. Lett. **24**, 131 (1984).
[3] Yu. M. Lugovoi, A. G. Shostenko, P. A. Zagorets, and V. P. Krapchatov, React. Kinet. Catal. Lett. **24**, 329 (1984).
[4] Yu. M. Lugovoi, A. G. Shostenko, P. A. Zagorets, and V. P. Krapchatov, React. Kinet. Catal. Lett. **24**, 335 (1984).

[5] N. Getoff, A. Ritter, and F. Schwörer, Radiat. Phys. Chem. **28**, 343 (1986).
[6] H. Ban, K. Sukegawa, and S. Tagawa, Macromolecules **20**, 1775 (1987).
[7] H. Ban, K. Sukegawa, and S. Tagawa, Macromolecules **21**, 45 (1988).
[8] N. Getoff, K. Kaindl, and E. H. Graul (eds): Strahlenchemie, pp. 226−249, Hüthig Verlag, Heidelberg (1967).