THE EFFECT OF HYDROGEN BROMIDE ON THE METHANE PRODUCTION IN THE GAMMA RADIOLYSIS OF THE H$_2$S-CH$_3$Br SYSTEM

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The influence of the HBr concentration on G/CH$_4$/ in the radiolysis of H$_2$S-CH$_3$Br system has been investigated. The rate constant for the formation of the double negative ion /CH$_3$Br.H$_2$S/- in the four body process was corrected.

Previously$^{1,2}$ we have shown that the thermal electrons react in the mixture of H$_2$S-CH$_3$Br with the double molecules of the van der Waals type such as /H$_2$S/$_2$ and /CH$_3$Br.H$_2$S/.

On the basis of the experiments with electron scavengers CCl$_4$ and CHCl$_3$ /Ref. 2/ we have proposed a mechanism of the electron attachment reactions in the system which can be written as follows:

\[
CH_3Br + H_2S \rightleftharpoons CH_3Br.H_2S /1a/ \\
e^- + CH_3Br.H_2S \rightarrow CH_3Br.H_2S^- /1b/ \\
\]

\[
/CH_3Br.H_2S^- + H_2S \rightarrow CH_4 + Products /1c/ \\
\]
Kinetically this set of reactions is identical with reaction /2/

\[ \text{e}^- + \text{CH}_3\text{Br} + 2\text{H}_2\text{S} \xrightarrow{k_2} \text{CH}_4 + \text{Products} \quad /2/ \]

and \( k_2 = K \cdot k_c \cdot k_s / k_a \) where \( K \) is the equilibrium constant of /CH\(_3\)Br.H\(_2\)S/ formation, \( k_c \) and \( k_a \) are the rate constants for the electron capture by the above complex and the autoionization of the ion, respectively, and \( k_s \) is the rate constant for the stabilization of the /CH\(_3\)Br.H\(_2\)S/-\( x \) excited ion.

The values of this rate constant as obtained from the experiments with CCl\(_4\) and CHCl\(_3\) differ ca. 3 times\(^2\).

The aim of this work was to get the value of this rate constant performing the experiment with hydrogen bromide. According to Nagra and Armstrong\(^3\) in the mixture of HBr-H\(_2\)S at the radiolysis conditions the electrons are attached forming double negative ion /HBr.H\(_2\)S/-\(^-\). They found out that the rate of this electron capture process depends on the pressure both of HBr and H\(_2\)S.

The experiment has been performed using the routine technique described elsewhere\(^4\). The concentration of the final product of the electron capture with methyl bromide, methane, was measured gas-chromatographically. The concentration of methyl bromide in the irradiated mixture with H\(_2\)S was high enough to capture all the electrons via reaction /2/ in the pure CH\(_3\)Br-H\(_2\)S system. The addition of hydrogen bromide to the system caused the decrease in the methane yield as it is shown in Fig. 1. It is seen that this decrease depends on the concentration of all components.

According to the results of Nagra et al.\(^3\) the process competing with reaction /2/ is reaction /3/

\[ \text{e}^- + \text{HBr} + \text{H}_2\text{S} \xrightarrow{k_3} /\text{HBr.H}_2\text{S/}^- \quad /3/ \]