Chemical Conversion of SO\textsubscript{2} in Low-Temperature and Low-Pressure Oxyhydrogen Flames.  
1. Kinetic Analysis of the Process

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**Abstract:** The chemical conversion of SO\textsubscript{2} to elemental sulfur in the chain oxidation of hydrogen in a low-temperature flame has been studied. The possible elementary reactions involving atoms and free radicals that may be responsible for the chemical conversion of SO\textsubscript{2} with the formation of sulfur in the conjugate radical chain process are discussed on the basis of thermodynamic and kinetic characteristics.

**Keywords:** sulfur, sulfur dioxide, chain reaction, free radicals, flame.

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**INTRODUCTION**

The problem of utilizing sulfur dioxide emitted into the atmosphere with the flue gases of thermal power plants and metallurgical plants motivates the search for rational pathways of its chemical conversion to harmless compounds. It has been found [1–3] that in low-temperature and low-pressure oxyhydrogen flames, a SO\textsubscript{2} additive undergoes chemical conversion to form elemental sulfur. These flames occur at a pressure $p \leq 200$ torr and a temperature of $T = 450–550^\circ$C, which corresponds to the region of the chain autoignition of oxyhydrogen mixtures. At the same time, this fact has not been observed in studies of the effect of SO\textsubscript{2} on the high-temperature combustion of various fuels, including hydrogen [4–13]. Under these conditions, as a rule, SO\textsubscript{2} has an inhibitory effect and, in some cases, also a promoting effect on the combustion process. Studies of the chain oxidation of hydrogen have shown that at relatively low temperatures and pressures, the addition of SO\textsubscript{2} reduces the rich flammability limit of oxyhydrogen mixtures [14].

It is interesting to note (see [1–3]) that sulfur dioxide undergoing a chemical conversion simultaneously affects the dynamics of low-temperature combustion of oxyhydrogen mixtures. Thus, at certain velocities of the gas mixture flow through the reactor, a new phenomenon is observed: transition of low-temperature combustion from the continuous flame regime to the intermittent flame regime, characterized by successive light flashes of particular frequency and intensity. The study of these flames is a separate independent problem.

This paper deals with the chemical conversion of sulfur dioxide to form elemental sulfur in the low-temperature combustion of hydrogen-rich oxyhydrogen mixtures. The possible chemical conversion pathways for SO\textsubscript{2} with the participation of the atoms and radicals formed in the chain oxidation of hydrogen. The enthalpy $\Delta H^0$ and Gibbs energy $\Delta G^0$ are calculated under standard conditions for each elementary step over a wide temperature range. The calculations were carried out using the NASA data for thermochemical properties [15]. The values of $\Delta H^0_{773}$ and $\Delta G^0_{773}$ at $T = 773$ K in combination with literature data on the rate constants were used to estimate the probability of a particular elementary reaction in low-temperature oxyhydrogen flames.

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EXPERIMENTAL

The experiments were conducted using a vacuum flow reactor. The mixture was prepared in advance in large glass flasks attached to a common glass reservoir. Gas mixture flows in the reactor were controlled by glass valves placed at the inlet and outlet of the reactor. The reactor made of quartz glass (volume 1250 cm$^3$, length 18.4 cm, and diameter 9.4 cm) was heated by a temperature-controlled electric furnace fitted with quartz observation windows on the side and at the end. The side window allows visual observation of the process over the whole volume of the reactor. A photosensitive receiver was placed in the end window, which transmitted signals from light flashes through an electronic transducer to a computer which continuously recorded signals.

The reaction products were subjected to chromatographic analysis. Hydrogen sulfide in appreciable quantities was not detected. Analysis for the SO$_3$ content was carried out by a nephelometric method and also gave a negative result. The resulting gas-phase sulfur was removed from the reactor by the reaction gas flow and settled in the trap and on the glass piping of the reactor, which were periodically cleaned. Samples from the trap were examined by x-ray diffraction analysis. For electron microscopic studies, small metal plates were placed in the pipelines directly behind the reactor outlet, and sulfur from the gas phase settled on these plates.

RESULTS AND DISCUSSION

The conversion of SO$_2$ in low-temperature and low-pressure oxyhydrogen flames were studied in the ranges $T = 450–510^\circ$C and $p \leq 200$ torr. These parameter ranges cover the region of chain autoignition of oxyhydrogen mixtures. Under flow conditions for these parameters, low-pressure flames occur. In the presence of SO$_2$ additives at certain flow velocities in the reactor (contact time $\tau \leq 1$ s), the process enters a new regime—the regime of intermittent flames (Fig. 1). Experiments have shown that in both regimes of low-pressure flames, SO$_3$ is transformed to elemental sulfur.

After leaving the reactor, gas-phase sulfur settled in the trap. X-ray diffraction analysis of powder sulfur taken from the trap showed that in all cases (for different values of $p$ and $T$) x-ray amorphous sulfur formed.