

NISTIR 6242

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Book of Abstracts
November 2-5, 1998

Kellie Ann Beall, Editor

Building and Fire Research Laboratory
Gaithersburg, Maryland 20899

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INHIBITION OF SILANE IGNITION BY IODINE CONTAINING ADDITIVES

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Silane is widely used in CVD processing in the semiconductor industry. The highly explosive nature of SiH₄-O₂ mixtures represents a serious safety problem. In this paper we report the results of numerical studies on the influence of iodine and hydrogen iodide additives on silane self-ignition limits. Previous studies of influence of different additives on silane combustion are summarized.

The kinetic model of silane combustion used in this work is based on previously suggested mechanisms for silane oxidation and pyrolysis. It is adjusted to fit recent experimental and theoretical studies for Si-containing species. The calculations are based on the Chemkin suite of programs.

The results of modeling show that the upper explosion limit of silane is determined by the balance of rates of a chain branching reaction (SiH₃ + O₂) and a termination process (H + O₂ + M = HO₂ + M). The critical pressure is proportional to the ratio of silane to oxygen concentration. The reactivity of the SiH₄-O₂ mixture increases monotonically with hydride content. Increase of the ratio SiH₄/O₂ at ambient conditions leads to chain ignition of silane mixtures. The experimentally observed violent explosion behavior of silane at ambient conditions is due to the very short ignition delay. In most cases ignition is observed during mixture preparation. With decrease of initial temperature (down to -100C) there might exist conditions for chain ignition for some local volume during mixture preparation. In spite of a very high value of a SiH₄/O₂ critical ratio and, correspondingly, low adiabatic temperature rises it is possible to expect that ignition will be observed for "favorable" (optimum) gradients of concentrations and ignition delay with decrease of initial temperature.

The analysis of the kinetic model demonstrates that the key radical intermediates are the same as those found in any hydrocarbon combustion system. Thus, the usual flame inhibitors should have similar inhibition effects. The consequence is that the hydrogen atoms and OH radicals generated from the chain-branching reaction of SiH₃+O₂ are removed and cannot attack silane. The results for the iodine system can be found in Fig. 1. The axes are concentrations of silane and O₂ and we define a boundary between regions where self-ignition exists or fails to occur. The drastic effect of iodine addition is readily seen. The effect of increasing iodine is to continually squeeze the region where ignition can occur. The simulations show the very high sensitivity of the silane ignition limit to iodine additive at the ppm level. At concentrations above 200 ppm iodine and ambient conditions silane is no longer pyrophoric. Increasing initial temperature leads to the increased range of self-ignition and leads to the need to increase the concentration of additive for the same level of inhibition.

The modeling of hydrogen iodide influence shows that much more is needed in order to obtain the same effect as iodine itself. Hydrogen iodide is a less effective inhibitor and concentrations of a factor of 10 higher than those for iodine are required. The effectiveness of iodine in comparison with other inhibitors is associated with the weakness of an iodine bond. Bond energy of I₂ is of the order of 160 kJ/mol. In contrast, the H-I bond strength is of order of 300 kJ/mol while that of the Si-H bond is approximately 390 kJ/mol. The rate constant for H+I₂ reaction is very large and is, roughly, an order of magnitude greater than those of H atom reactions with other halogenated and nonhalogenated hydrocarbon additives at room temperature.

The critical conditions for chain ignition can be deduced using an abbreviated kinetic scheme.

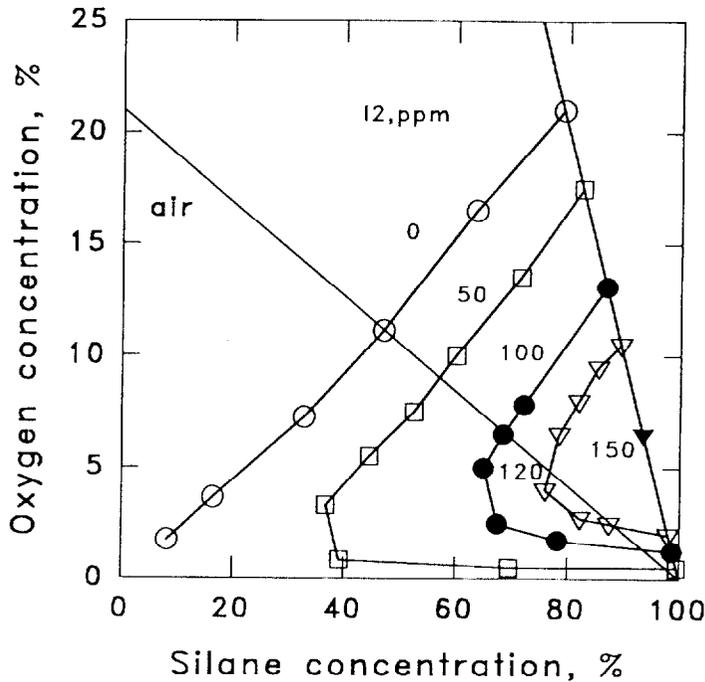
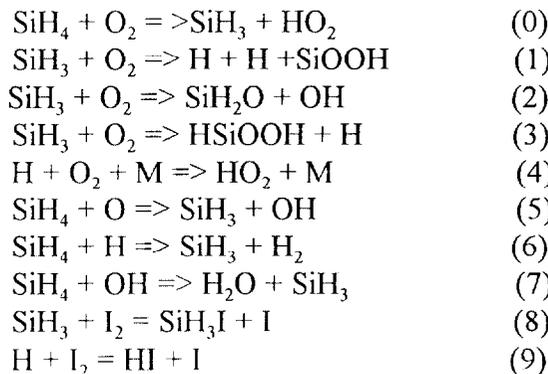


Figure 1. Self-ignition limits for silane/oxygen/nitrogen mixtures for various amounts of added iodine at 1 atm and 300 K.

The simplified mechanism is



The following relation for the critical pressure for the uninhibited upper explosion limit as a function of temperature and SiH_4 and O_2 concentrations is obtained

$$M = [K_1 K_6 / (K_4 (K_1 + K_3))] * (\text{SiH}_4 / \text{O}_2) .$$

The formula shows that critical pressure depends on the ratio of silane and oxygen concentrations. The critical pressure for the upper explosion limit inhibited by I_2 is the following

$$M = [K_1 K_6 (\text{SiH}_4 / \text{O}_2) - K_8 K_6 (\text{I}_2 / \text{O}_2)] / [K_4 (K_1 + K_3 + K_8 (\text{I}_2 / \text{SiH}_4))] - (K_9 / K_4) (\text{I}_2 / \text{O}_2) .$$

The analysis of this formula and simulation results show that there exist two critical values of the ratio of silane concentration to oxygen concentration (Fig 1).

The important result from this work is that pyrophoric properties of silane and inferentially other pyrophoric hydrides can be significantly changed through the use of quite small amounts of additives and this may well lead to reductions in hazards arising from the handling of such substances. This is because in many of these cases the key intermediates are the small inorganic radicals that play a key role in hydrocarbon combustion.