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AN EXPERIMENTAL AND THEORETICAL STUDY OF FLAME INHIBITION
BY BROMINE-CONTAINING COMPOUNDS

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Introduction

Flame inhibition by halogenated compounds is an important problem having great practical and theoretical interest. Experimentally, inhibition and retardance of flames has been observed for many years, and the properties of many different inhibitors have been catalogued. With halogenated species, it is well known that bromine and iodine are substantially more effective inhibitors than are chlorine or fluorine. In addition, the rate of inhibition is roughly proportional to the number of halogen atoms present, so that CHBr_3 , CBr_2Br_2 , and CH_2Br_2 reduce the flame speed in methane-air approximately in the ratio 3:2:1 [1]. Relatively little detailed kinetic modeling work on flame inhibition has been carried out. Dixon-Lewis and co-workers [2-4] studied H_2 -air flames inhibited by HBr , and Westbrook has examined methane-air and methanol-air flames inhibited by HBr [5] and by CH_3Br [6]. The present paper represents the first effort to date in which a combined experimental and theoretical approach has been used to study the effects of several inhibitors on hydrocarbon-air flames. This work is part of an attempt to build a consistent picture of chemical kinetic flame inhibition, beginning with a simple halogen molecule such as HBr and progressing sequentially towards more complex and more practical inhibitors such as CF_3Br .

Measurement technique and instrumentation

Acoustically stabilized flat propagating flames are used to measure laminar flame speed in premixed fuel-air gases with and without halogenated gas phase inhibitors. The technique [7] involves measuring the downward propagation rate of a flame in a quartz tube with a polaroid camera, shuttered by a 300 rpm sectored disc. Flat flame fronts result when a flame-driven resonance is established between the bottom of the tube and a screened orifice at an empirically determined location above the igniting spark gap [8].

Combustible gas mixtures are prepared, assuming that all mixture gases are in temperature equilibrium. Thus the ratio of partial pressure of each gas to the pressure of the total mixture is also the ratio of its volume to the volume of the total mixture. Mixing is accomplished by successively adding the desired gases to an insulated mixture tank until its

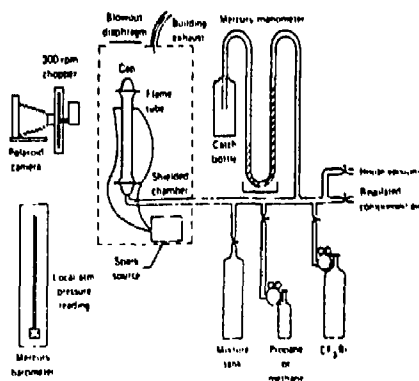


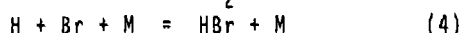
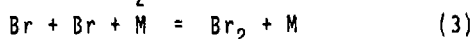
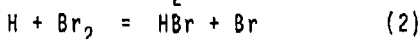
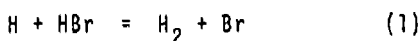
Figure 1

absolute pressure increases to a final mixture pressure of nearly 2 atm. We insulate the mixture tank to ensure its temperature remains constant during the mixing process. Before adding each gas, we evacuate and purge the manifold and lines leading to the mixture tank. Once each gas is added to the tank, we assure mixture uniformity by repeatedly inverting the tank and by allowing sufficient time before testing for thorough mixing by diffusion. After the mixture is established in the mixture tank, we introduce it (via the manifold) into the evacuated flame tube. When the manometer indicates atmospheric pressure in the flame tube, we activate the diagnostic circuits, remove the top cap of the flame tube and turn on the spark source. The test apparatus is shown schematically in Figure 1. In the present series of experiments methane-air mixtures were studied, with HBr and CH_2Br inhibitors in varying amounts. Results with CF_3Br inhibitor in the same apparatus have been reported previously [8].

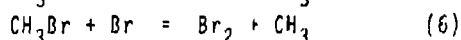
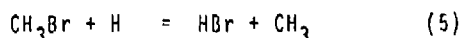
Numerical flame modeling

The numerical model used in this work was developed by Lund [9] and has been used in previous studies of flame propagation and inhibition [5,6,10,11]. The equations of conservation of mass, momentum, and energy are solved simultaneously with the chemical species conservation equations including the kinetics terms, in a planar one-dimensional configuration. All transport coefficients and thermodynamic data have been validated in earlier studies and are used here without modification.

The reaction mechanism combines an extensive model for the oxidation of simple hydrocarbons (CH_4 , CH_3OH , C_2H_4 , C_2H_6) with a mechanism for the reactions of species containing Br atoms. The specific reactions and their rates are not reproduced here due to limitations in space but are reviewed in detail in the references [5,10]. Although other reactions of Br, HBr, and Br_2 are included, the most important reactions involving these species are:



Species such as BrO and BrOH are not included. As a first approximation it is assumed that the principal reactions of CH₃Br involve abstraction of the Br atom only, through



followed by conventional reactions of the methyl radicals. Reactions abstracting H atoms from methyl bromide and subsequent reactions involving CH₂Br, CHBr and CBr are not considered in this mechanism. This mechanism, combined with the hydrocarbon oxidation mechanism, has been shown [5,6] to reproduce available flame propagation and inhibition data with HBr and CH₃Br inhibitors. Future additions will include elementary reactions dealing with CF₃Br and its intermediates.

Discussion

The general picture of kinetic flame inhibition which is predicted by the numerical model consists of a catalyzed recombination of hydrogen atoms, removing them from the induction and reaction zones of the flame. Hydrogen atoms removed in this manner are then unavailable for the key chain branching reaction $\text{H} + \text{O}_2 = \text{O} + \text{OH}$, leading to a reduced rate of fuel consumption, heat release, and flame propagation. The H atom recombination is catalyzed by Br through reactions 1-4. Methyl bromide acts primarily as a source of Br atoms which then inhibit the flame through the same HBr mechanism. HBr and CH₃Br do not act in exactly the same way; the C-Br and H-Br bond energies are different, so the temperature dependence of reactions 1, 2, 5, and 6 are not the same. Furthermore, the addition of CH₃Br to a given methane-air mixture produces a slight shift in the overall fuel-air equivalence ratio in the rich direction which can also affect the flame speed. Still, computed flame speeds with HBr inhibitor are found to be very nearly equal to those computed with CH₃Br inhibitor.

Experimental flame speed measurements were generally consistent with the computed results, although several problems made it difficult to obtain precise values for the flame speed in some cases. With HBr-CH₄-air mixtures, rapid deterioration of the HBr through reaction with the walls of the storage tank made it impossible to carry out a second chemical analysis of the reactive mixture composition subsequent to the flame speed measurements. Compressibility of CH₃Br in the manifold and lines produced uncertainties in the composition of the CH₃Br-CH₄-air mixtures. In both cases the flame speed measurements themselves are accurate and highly repeatable, with the uncertainties resting primarily on the possible errors in

specifying the exact mixture composition. Improved equipment and techniques involving heated lines and mixing tank may reduce these uncertainties, but the trends which are observed in the numerical results were confirmed by the experiments.

The inhibitors used, HBr and CH_3Br , were found to be almost equally effective in their ability to reduce the laminar flame speed. With both inhibitors the numerical model predicts an increased inhibition efficiency for fuel-lean mixtures. This is a result of the lower H atom concentration in the front portion of the flame ($1000\text{K} \leq T \leq 1500\text{K}$) for lean flames. Therefore the addition of a given quantity of inhibitor has a proportionally greater effect in these lean flames. Stoichiometric and rich flames have an ample supply of H atoms and are not as sensitive to a partial depletion of them due to inhibitor addition. This effect could not be resolved in the latest experiments with HBr or CH_3Br , but earlier results with CF_3Br [8] as inhibitor in CH_4 -air and C_2H_6 -air flames clearly demonstrated the increased effectiveness of inhibition for fuel-lean flames. The same trend should be observed in the efficiency of inhibition for all fuel-air mixtures in which the reaction $\text{H} + \text{O}_2 = \text{O} + \text{OH}$ plays a central role, including flames of other more complex hydrocarbons and of ammonia.

Inhibition efficiency can be defined as the rate of flame speed reduction, the amount of flame speed change per unit inhibitor added ($-dS_f/dX_i$, with S_f the flame speed and X_i the inhibitor mole fraction). Both the numerical model and the flame tube measurements found that the inhibition efficiency gradually decreases as the amount of inhibitor is increased, as shown in Figure 2. The present experimental and modeling results are shown, together with earlier data for $\text{CF}_3\text{Br}-\text{CH}_4$ -air and $\text{CF}_3\text{Br}-\text{C}_2\text{H}_6$ -air [8] as well as HBr- CH_4 -air, $\text{CH}_3\text{Br}-\text{CH}_4$ -air and $\text{CF}_3\text{Br}-\text{CH}_4$ -air [1]. In the numerical study it was found that a stoichiometric methane-air mixture with up to 8% methyl bromide could support a flame, propagating at a speed of about 5 cm/sec, even though the addition of the first 1% of CH_3Br had reduced the flame speed from 38 cm/sec to about 26 cm/sec.

Extensions of the model to include CF_3Br are currently under development. The available experimental data suggest that CF_3Br is somewhat more efficient as an inhibitor than HBr or CH_3Br . This is due primarily to the fact that the fluorine atoms permanently remove H atoms from the flame through the formation of HF, which is much less reactive than its analog HBr. Since these H atoms never are returned to the flame, the rate of chain initiation and branching throughout the flame is lower and the Br atoms have a larger proportionate effect, similar to the situation prevailing in fuel-lean flames as discussed above.

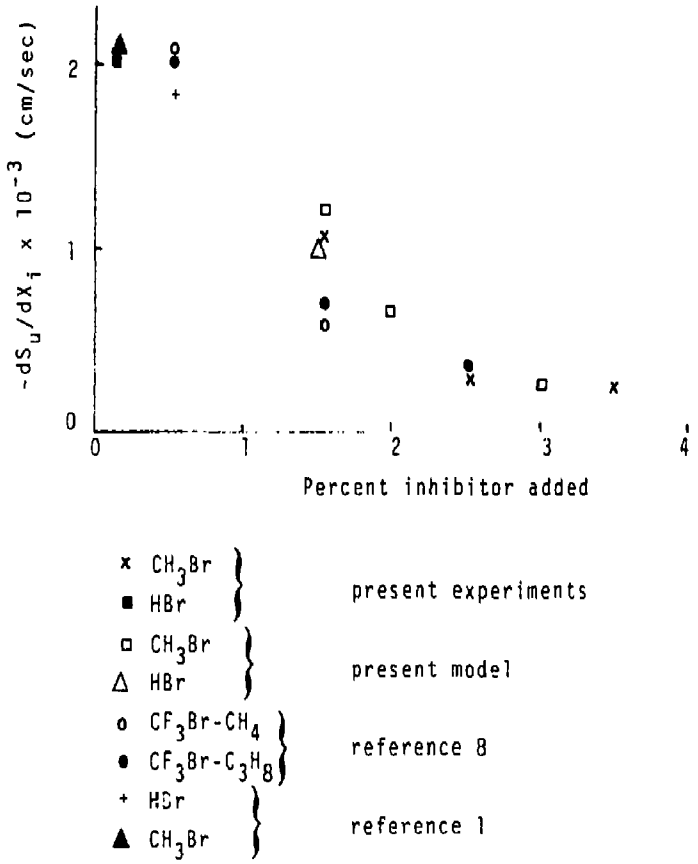


Figure 2

Acknowledgements

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