

*Dedicated to the memory of  
Professor Petru Spacu (1906–1995)*

## INHIBITION OF PREMIXED C<sub>3</sub>H<sub>6</sub>-AIR FLAMES BY CH<sub>2</sub>BrCl

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The effect of gaseous CH<sub>2</sub>BrCl addition upon the characteristic parameters of combustion propagation in propylene-air mixtures in a closed vessel was investigated, at various initial pressures within 0.3-1.3 bar and various [C<sub>3</sub>H<sub>6</sub>] : [O<sub>2</sub>] and [C<sub>3</sub>H<sub>6</sub>] : [CH<sub>2</sub>BrCl] ratios. Small concentrations of added CH<sub>2</sub>BrCl (0.5-1.0 vol %) to propylene – air mixtures do not influence much the peak explosion pressures, as CH<sub>2</sub>BrCl contributes to the total amount of released heat. An important inhibiting effect of the additive is observed by means of normal burning velocities and rates of pressure rise, directly influenced by the overall reaction rate in the flame front.

### INTRODUCTION

The inhibiting effect of halogenated hydrocarbons on fuel-air flames is known since long and extensively studied.<sup>1-12</sup> Very small concentrations of such additives (even below 1%) in a hydrocarbon-air flame determine a significant lowering of burning velocity, in comparison with hydrocarbon-air flames without additive. Typical examples are Halon 1301 (CF<sub>3</sub>Br) and most of fluoroderivatives of C<sub>1</sub>- and C<sub>2</sub>-hydrocarbons.<sup>5-10</sup> The influence of inhibitors on burning velocity of fuels was explained mainly by a chemical mechanism: the inhibitor acts as a radical scavenger, reducing the total concentration of chain carriers.<sup>1-3, 7-10</sup> At inhibitor concentrations higher than 1%, the physical mechanism is also effective: the additive determines the change of heat capacity and thermal conductivity of the gaseous mixture, which determine the change of flame temperature and accordingly, of overall reaction rate and burning velocity.<sup>7-10</sup>

Many studies, both experimental and computational, were focused on the quantitative characterization of inhibiting effect, i.e. the correlation between additive concentration and burning velocity, for various fuels and/or inhibitors.<sup>1,4,7,8,10</sup> For CH<sub>4</sub>-air flames doped with various inhibitors with concentrations lower than 0.5 vol. %, Rosser, Wise and Miller found a linear correlation between the burning velocity and additive concentration.<sup>1</sup> For a wider additive concentration range, up to the extinguishing concentration, a nonlinear dependence of the burning velocity on inhibitor concentration was found.<sup>7,8,10</sup> A complex influence of the inhibitor was thus revealed, both on flame temperature and total radical concentration. Noto, Babushok, Hamins and Tsang<sup>7</sup> suggested a procedure to differentiate between the physical and chemical contributions of various inhibitors and found that the increase of inhibitor concentration leads to saturation of its chemical contribution. A subsequent increase of inhibitor action is determined entirely by physical factors (heat capacity and dilution effects).

Besides burning velocity, other explosivity parameters are also important from the point of view of safety recommendations: the flammability limits and the limiting oxygen concentration, the peak pressures, the times necessary to reach the peak pressures and the maximum rates of pressure rise reached in closed vessel explosions. Such parameters are worth to be examined, since halogenated hydrocarbons are themselves fuels able to support the propagation of an autonomous flame.<sup>13-16</sup> Most reported values refer to the influence of halogenated hydrocarbons on the flammability range of fuel-air mixtures at ambient conditions.<sup>17-21</sup> A comprehensive set of

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critical inerting concentrations of various suppressants towards several stoichiometric fuel-air mixtures is given by Babushok and Tsang,<sup>10</sup> according to recent measurements in cup burners.

In the present paper, data on the explosive combustion of propylene-air mixtures doped with small variable amounts of  $\text{CH}_2\text{BrCl}$  are reported. The experiments, performed in a closed spherical vessel with central ignition, were run in deflagration regime, at ambient initial temperature and variable initial pressure within 0.3 and 1.3 bar. The process was characterized by the peak pressures, the times necessary to reach the peak pressure, the maximum rates of pressure rise and the normal burning velocities, at various initial pressures. Bromochloromethane, less studied as inhibitor of hydrocarbon-air flames, was chosen due to its satisfactory volatility, at ambient temperature. Lean mixtures propylene-air and (propylene with inhibitor)-air were studied. The reason was to avoid combustion in a deficit of oxygen, maintaining thus a restricted number of combustion products, as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{Br}_2$  and  $\text{Cl}_2$ , together with nitrogen and the unburned oxygen. Since the calculation of an equivalence ratio is difficult in case of mixed fuels, we compared the flammability parameters of studied (propylene with inhibitor)-air mixtures with those referring to propylene-air mixtures having the same mole number of unburned oxygen per total mole number of fuel.

## EXPERIMENTAL PART

The explosion vessel was a stainless steel spherical bomb of 10 cm inner diameter, fitted with stainless steel electrodes; the spark gap was located in the bomb centre. Electric sparks produced by a standard automotive induction coil were used for explosion initiation. The pressure variation during flame propagation was monitored by means of a piezoelectric pressure transducer (Kistler 601A) coupled with a Charge Amplifier Kistler 5001 SN. The signal was recorded and stored by a digital acquisition data system Tektronix TestLab 2505, usually at 5000 signals/s. Other characteristics of the experimental set-up were previously given.<sup>22-24</sup>

The explosive mixtures were obtained by partial pressure method, in 10 L steel cylinders, at 4 bar total pressure. The additive which is liquid at room temperature was vaporized before mixing with air, by injecting the liquid into a spherical bulb evacuated at 0.1 mbar, through a side tube having a vacuum-tight injection septum at its end.

The experiments were performed at ambient temperature and various total initial pressures within 0.3 and 1.3 bar.

Propylene (ARPECHIM-Pitesti), 99.0% and  $\text{CH}_2\text{BrCl}$  (Merck, Germany), p.a. were used without further purification. Air was dried by means of a line containing  $\text{H}_2\text{SO}_4$ , KOH (s),  $\text{CaCl}_2$  and silicagel with moisture indicator.

## RESULTS AND DISCUSSION

The presence of  $\text{CH}_2\text{BrCl}$  even in low concentration (0.5 and 1.0 vol.%) in propylene-air mixtures determines the decrease of both peak pressure and maximum rate of pressure rise and an increase of time to peak pressure, as seen from a few oscillograms given in Fig. 1. The data represent the pressure evolution during the explosions of a (3.93  $\text{C}_3\text{H}_6$  + 0.5%  $\text{CH}_2\text{BrCl}$ )-air mixture, at two values of initial pressures  $p_0$ , in comparison with similar data referring to a 4.11%  $\text{C}_3\text{H}_6$ -air mixture.

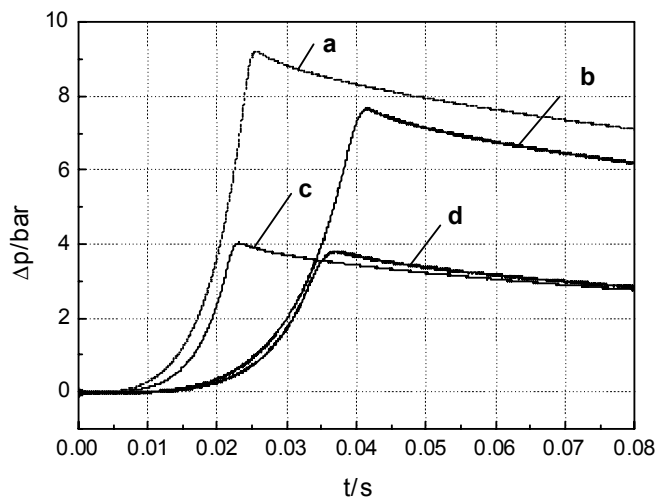


Fig. 1 – Pressure variation during explosions in a spherical vessel  
 (a)  $\text{C}_3\text{H}_6$ -air,  $p_0 = 1.0$  bar; (b)  $(\text{C}_3\text{H}_6 + 0.5\% \text{CH}_2\text{BrCl})$ -air,  $p_0 = 1.0$  bar;  
 (c)  $\text{C}_3\text{H}_6$ -air,  $p_0 = 0.5$  bar; (d)  $(\text{C}_3\text{H}_6 + 0.5\% \text{CH}_2\text{BrCl})$ -air,  $p_0 = 0.5$  bar.

In Table 1, the characteristic parameters of deflagrative explosions in a spherical vessel at various initial pressures (the peak pressure  $p_{max}$ , the time necessary to reach the peak pressure  $\theta_{max}$  and the maximum rate of pressure rise  $(dp/dt)_{max}$ ) are listed, for a lean propylene-air mixture doped with 0.5%  $\text{CH}_2\text{BrCl}$ . Similar results, obtained for a mixture containing (4.03%  $\text{C}_3\text{H}_6$  + 1.0%  $\text{CH}_2\text{BrCl}$ ) in air, are plotted versus initial pressure  $p_0$  in Figures 2 and 3, together with data referring to the stoichiometric propylene-air mixture. For both mixtures containing  $\text{CH}_2\text{BrCl}$ , the peak pressures are closed to peak pressures determined in the reference propylene-air mixture, since the additive itself is a fuel which contributes to the total combustion heat, released during the explosion.

Table 1

Characteristic parameters of explosion in a spherical vessel for a  
(3.93%  $\text{C}_3\text{H}_6$  + 0.5%  $\text{CH}_2\text{BrCl}$ ) -air gaseous mixture, at various initial pressures

$p_0$ /bar	$\Delta p_{max}$ /bar	$\theta_{max}$ /ms	$(dp/dt)_{max}$ /( $\text{bar}\cdot\text{s}^{-1}$ )
0.451	3.421	37.01	349.0
0.501	3.182	40.03	365.7
0.600	4.594	41.30	459.2
0.700	5.337	40.55	509.3
0.701	5.443	36.85	522.6
0.702	5.401	38.40	548.8
0.800	6.168	38.80	591.7
0.900	6.926	39.90	667.5
1.000	7.678	41.50	709.2
1.101	8.499	41.20	807.0

Large differences are observed between the maximum rates of pressure rise, in propylene-air mixtures with and without inhibitor (Fig. 1 and Fig. 3) and between the times necessary to reach the peak pressure (Fig. 1). Addition of  $\text{CH}_2\text{BrCl}$  to propylene-air mixture has a great influence on the heat release rate, determined mainly by the overall reaction rate. This supports the inhibiting effect of halogen derivatives towards the chain branching reactions.<sup>3,12,14</sup> Similar effects were reported by Shebeko et al. who investigated the explosion of  $\text{H}_2$ -air and  $\text{CH}_4$ -air mixtures in closed vessel, in the presence of several fluorinated hydrocarbons.<sup>9</sup> In stoichiometric and rich-fuel mixtures addition of a halogenated hydrocarbon determined the decrease of both peak pressures and rates of pressure rise. In a few cases, however, addition of 2-3 % fluorinated hydrocarbon to lean  $\text{CH}_4$ -air mixtures, determined the increase of peak pressure and pressure rise rate, since the supplementary amount of fuel consumed all available oxygen and brought the system to the stoichiometric composition.

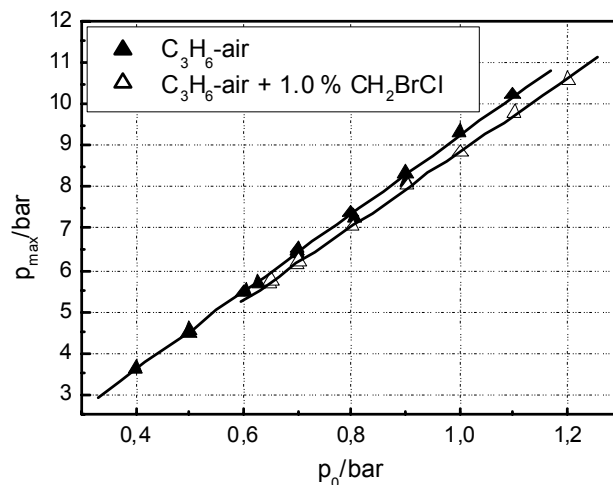


Fig. 2 – Peak pressures of deflagrations in a spherical vessel with central ignition  
(▲) 4.46%  $\text{C}_3\text{H}_6$ -air; (Δ) (4.03%  $\text{C}_3\text{H}_6$  + 1.0%  $\text{CH}_2\text{BrCl}$ )-air.

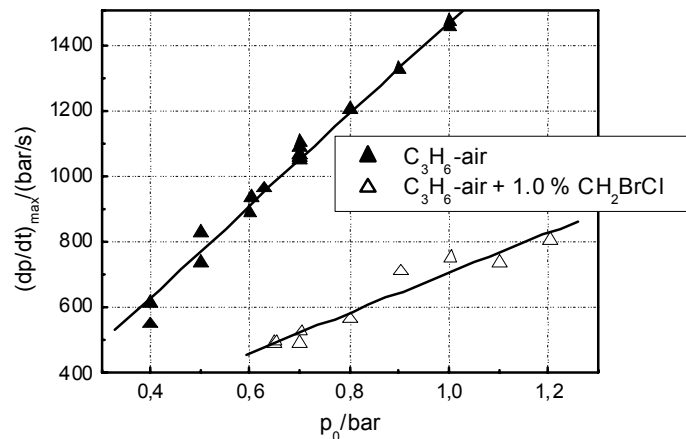


Fig. 3 – Maximum rates of pressure rise in a spherical vessel with central ignition (▲) 4.46%  $C_3H_6$ -air; (Δ) (4.03%  $C_3H_6$ +1.0%  $CH_2BrCl$ )-air.

Other data refer to a stoichiometric propylene-air mixture doped with 1%  $CH_2BrCl$  ( $[C_3H_6]/[CH_2BrCl] = 4$ ), stepwise diluted with air until ignition was no more observed. The results are plotted in Figures 4 and 5, together with data referring to  $C_3H_6$  – air without  $CH_2BrCl$ . Addition of excess air to a stoichiometric mixture of ( $C_3H_6 + CH_2BrCl$ ) mixture 4 : 1 or to a stoichiometric mixture  $C_3H_6$  – air (the lean propylene-air mixtures can be considered as a stoichiometric mixture diluted with excess air) determines the decrease of both peak pressure and rate of pressure rise. Only a physical dilution effect is present, when the decrease of fuel amount determines the decrease of evolved heat and the rate of heat release, as well.

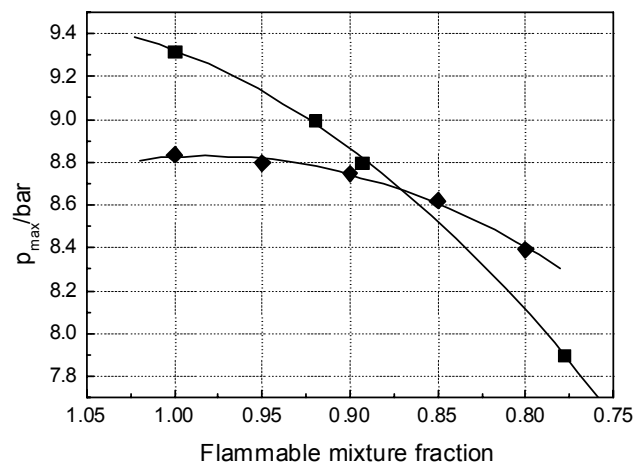


Fig. 4 – Peak pressures of deflagrations in a spherical vessel, at  $p_0 = 1$  bar; (◆) stoichiometric ( $C_3H_6 + 1.0\% CH_2BrCl + air$ ) mixture, diluted with air (■) stoichiometric ( $C_3H_6 + air$ ) mixture, diluted with air.

The analysis of pressure evolution during the early stage of the closed vessel explosion revealed the validity of the cubic law of pressure variation against time, for all fuel-air systems doped with  $CH_2BrCl$ . The constants  $k_2$  of the cubic law, written as:

$$\Delta p = k_1 + k_2 (t - k_3)^3 \quad (1)$$

were evaluated by a nonlinear regression method, for all investigated systems. The constants  $k_2$  were used to calculate the normal burning velocities  $S_u$  of flammable mixtures according to a simplified model of

flame propagation in the early stage of explosion,<sup>23</sup> using the following equation:

$$k_2 = (p_{\max} - p_0) \left( \frac{p_{\max}}{p_0} \right)^2 \frac{S_u^3}{R^3} \quad (2)$$

where  $p_{\max}$  is the peak pressure reached in the explosion of a gaseous mixture in a vessel with radius  $R$ , at initial pressure  $p_0$ . A typical set of data is given in Table 2.

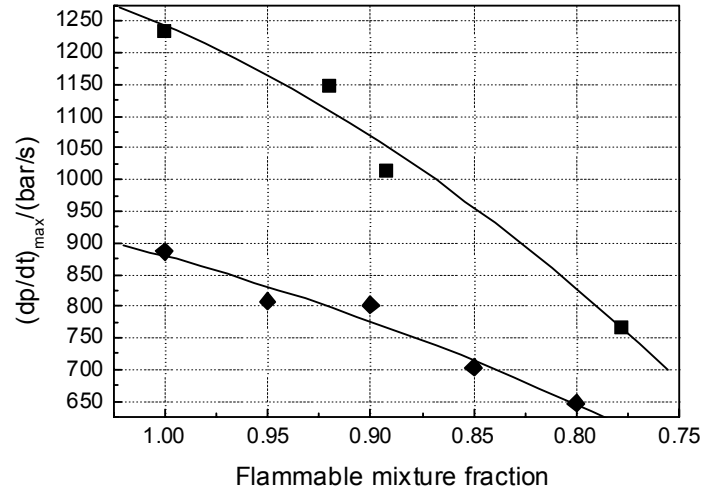


Fig. 5 – Maximum rates of pressure rise in a spherical vessel with central ignition, at  $p_0 = 1$  bar;  
 (●) stoichiometric ( $C_3H_6 + 1.0\% CH_2BrCl + air$ ) mixture, diluted with air;  
 (■) stoichiometric ( $C_3H_6 + air$ ) mixture, diluted with air.

Burning velocity variation against pressure, for  $CH_2BrCl$ -doped systems as compared to non-doped systems, is given in Fig. 6. Within the examined pressure range, addition of halogenated compound leads to an important decrease of burning velocity. Thus, system 1 can be compared with system 2 and system 3 with system 4 (their compositions are listed in Table 2). The same effect is observed in systems having a constant mole ratio  $[C_3H_6]/[CH_2BrCl]$  (mixtures 5 - 8 from Table 2), obtained from mixture 4 by progressive dilution with air.

Table 2

Peak pressures, cubic law constants and normal burning velocities of ( $C_3H_6 + CH_2BrCl$ )-air mixtures with variable  $C_3H_6$  and  $CH_2BrCl$  content, at constant initial pressure  $p_0 = 1$  bar.

Nr.	$[C_3H_6]/(vol\%)$	$[CH_2BrCl]/(vol\%)$	$p_{\max}/bar$	$k_2 \cdot 10^4 / (bar \cdot s^{-3})$	$S_u / (cm/s)$
1	4.11	-	9.32	47.59	43.5
2	3.93	0.50	8.75	12.36	29.4
3	4.46	-	9.23	54.74	46.0
4	4.03	1.00	8.75	12.98	30.2
5	3.83	0.95	8.80	12.81	29.8
6	3.63	0.90	8.75	8.68	26.4
7	3.43	0.85	8.62	6.69	24.5
8	3.22	0.80	8.40	5.42	23.6

The inhibiting effect of  $CH_2BrCl$  on propylene-air flames, as seen from burning velocity values, could be assigned to both Br and Cl atoms. Numerical computations of burning velocity for several fuel-air flames doped with 1 vol. % halogen acids or mono-halogenated hydrocarbons have shown that halogen atoms catalyze the recombination of H atoms to  $H_2$  molecules, having a much lower reactivity.<sup>3</sup> By such action,

they diminish the available radical pool and lower the overall rate of chain branching. In this respect, Cl atoms are much less effective than Br atoms, which are only slightly less effective than I atoms. Based on such evaluation, we may ascertain the influence of  $\text{CH}_2\text{BrCl}$  on  $\text{C}_3\text{H}_6$ -air flames only to Br atoms. A comparison between burning velocities of several doped flames is given in Table 3. Indeed, all listed inhibitors determine, by means of Br atoms, a significant decrease of burning velocity.

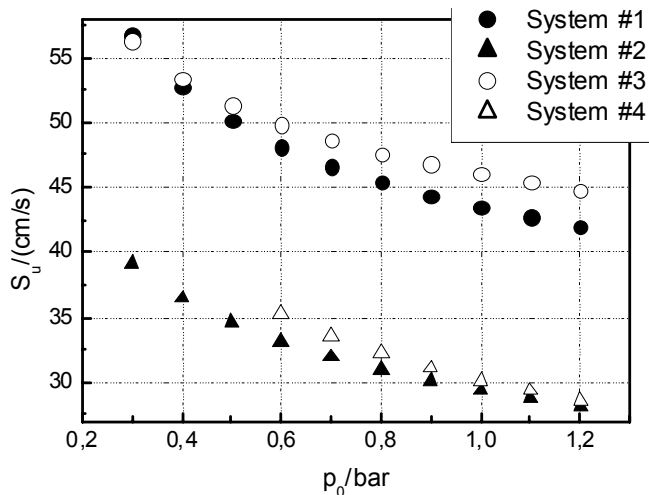


Fig. 6 – Burning velocities of propylene- $\text{CH}_2\text{BrCl}$ -air mixtures, at  $p_0 = p_{atm} = 1$  bar.  
 (○) 4.46%  $\text{C}_3\text{H}_6$ -air; (△) (4.03%  $\text{C}_3\text{H}_6$ +1.0%  $\text{CH}_2\text{BrCl}$ )-air;  
 (●) 4.11%  $\text{C}_3\text{H}_6$ -air; (▲) (3.93%  $\text{C}_3\text{H}_6$ +0.5%  $\text{CH}_2\text{BrCl}$ )-air.

Table 3

Influence of various additives containing halogen on burning velocity of fuel-air mixtures, at  $p_0 = 1$  bar and  $T_0 = 298$  K. Additive concentration: 1 vol %.

Fuel	Inhibitor	$S_u$ / (cm·s <sup>-1</sup> )	Source of data
$\text{CH}_4$	none	36	3
$\text{CH}_4$	HBr	24	3
$\text{CH}_4$	$\text{CH}_3\text{Br}$	26	3
$\text{CH}_4$	$\text{C}_2\text{H}_3\text{Br}$	27	3
$\text{C}_2\text{H}_4$	none	70	3
$\text{C}_2\text{H}_4$	HBr	60	3
$\text{C}_2\text{H}_4$	$\text{CH}_3\text{Br}$	61	3
$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_3\text{Br}$	61	3
$\text{C}_3\text{H}_6$	none	46	Present paper
$\text{C}_3\text{H}_6$	$\text{CH}_2\text{BrCl}$	30	Present paper

## CONCLUSIONS

The experimental study of flame propagation in a spherical vessel with central ignition, performed with propylene-air and propylene-air doped with gaseous  $\text{CH}_2\text{BrCl}$  revealed a strong influence of the halogenated hydrocarbon on several characteristic propagation parameters: the time necessary to reach the peak pressure, the maximum rate of pressure rise and the normal burning velocity, even at concentration below 1 vol %. The presence of  $\text{CH}_2\text{BrCl}$  does not influence significantly the peak pressure, as the additive itself is a fuel, contributing to the total combustion heat.

The most important effect of the additive is the decrease of the reaction rate in the flame front, which accounts for the decrease of burning velocity, of maximum rate of pressure rise and for the increase of time necessary to reach the peak pressure.

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