On chemical inhibition of shock wave ignition of hydrogen–oxygen mixtures

A V Drakon¹, A V Eremin¹ and E Yu Mikheyeva¹,²
¹ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
² Bauman Moscow State Technical University, 2nd Baumanskaya Street 5, Moscow 105005, Russia
E-mail: drakon.a.v@gmail.com

Abstract. In this work an influence of the wide range of various inhibitors, namely CCl₄, CF₃H, C₂F₄Br₂, (CH₃O)₃P, CF₃I and C₃F₇I on shock-induced ignition of hydrogen was experimentally investigated. Observed temperature dependencies of induction times indicates that CF₃H and (CH₃O)₃P do not show noticeable inhibiting activity at given conditions, while the effectiveness of halogen-containing specie dramatically increases in a row Cl → Br → I. It is shown that the most effective inhibitors of ignition of hydrogen–oxygen mixtures are iodinated hydrocarbons CF₃I and C₃F₇I.

1. Introduction
The prevention of catastrophic explosions of hydrogen (particularly during the accidents at nuclear power plants) is the actual problem for existing and developing energy technologies. An introduction of chemically active inhibitors which suppress the combustion and detonation development is widely considered. It is known that their effectiveness is caused not only by the removal of oxygen from the fire zone and the high endothermic effect of their evaporation and dissociation, resulting in a temperature reduction in the combustion zone, but also by their chemical reactivity. The generalized mechanism for the chemical inhibition of ignition proposed in the classical paper [1] relates the flame-retardant effect to the reactions

\[
O + X + M \rightarrow OX + M, \quad (1)
\]

\[
O + X₂ \rightarrow OX + X, \quad (2)
\]

\[
RX + H \rightarrow HX + R \quad (3)
\]

(X is halogen), which result in binding of active radicals of O, OH, and H and their substitution with less active radicals R. Thus, reactions (1)–(3) compete with the chain reactions

\[
H + O₂ \rightarrow OH + O, \quad (4)
\]

\[
O + H₂ \rightarrow OH + H, \quad (5)
\]

\[
OH + H₂ \rightarrow H₂O + H, \quad (6)
\]

and inhibit the development of combustion. However, it was noted already in [1], that under certain conditions, chemically active admixtures may lose their flame-retardant properties and even lead to a reduction in the ignition delay. In the recent papers, it has been shown that
at elevated temperatures, halogenated and phosphorus-containing fire suppressants can reduce the ignition delay in methane-oxygen mixtures [2–5], accelerate detonation in acetylene [6], and, moreover, are themselves capable of combustion [7]. Experimental studies on the ignition of haloalkane-containing mixtures in a wide range of parameters can support the development of a comprehensive model of pyrolysis and oxidation of haloalkanes and their influence of combustion development. This is also a scientific task for the development of modern fire extinguishing systems and the analysis of industrial risks.

One should note that shock tube experiment differ fundamentally from other types of experiments such as initiation of ignition at room temperature by a local energy source, or the study of thresholds and the rates of flame propagation. In these conditions the processes of heat conductivity and diffusion of the active radicals play the main role, while ignition in a shock tube occurs at the total homogeneity of process in the volume and completely defined by kinetics of chain reactions. Therefore, only experiments behind shock waves allow the most reliable study of the kinetic mechanisms of the effect of various inhibitors on the ignition of hydrogen.

Therefore, the goal of this work was to perform an experimental and numerical study of the effect of various flame-retardant additives, namely CCl₄, CF₃H, C₂F₄Br₂, (CH₃)₃P, CF₃I and C₃F₇I, on hydrogen–oxygen mixtures ignition behind shock waves of different intensity.

Carbon tetrachloride, also known as Halon-104, was used in the beginning of the twentieth century, but was later rejected because of its noticeable toxicity. Lately other, safer halogenoalkanes, particularly fluoroform CF₃H (Freon-23) [8] and 1,2-dibromoperfluoroethane C₂F₄Br₂ (Freon-114B2) [9], were considered as agents to prevent the explosion and detonation of combustible mixtures and were widely used in fire-extinguishing systems. Nowadays, many halogenated compounds are considered toxic, ozone-depleting gases and forbidden by Montreal Protocol. Therefore it is recommended to use more safe iodinated hydrocarbons such as CF₃I and C₃F₇I. One should note, though, that brominated hydrocarbons still can be applied for rare emergency use on unmanned facilities such as nuclear reactors containments if their effectiveness is high enough. Phosphorus-containing compounds such as trimethylphosphite (CH₃O)₃P are another promising, but much less studied type of chemical reagents which were shown to be effective flame retardants for hydrocarbons [10–13], syngas [14], and hydrogen [15].

2. Experimental and modeling methods

Experiments were carried out in stainless steel shock tube of standard design in stoichiometric hydrogen–oxygen mixtures diluted with argon to 10–20% and doped with 1–3% of studied suppressants. The investigated section had optical windows and was located at a distance of 13 mm from the end plate. The shock tube was equipped with several PCB113B piezoelectric pressure gauges to measure the incident shock wave velocity with an accuracy 0.5%. The actual values of temperature ($T_{RSW}$) and pressure ($P_{RSW}$) of shock-heated flow behind reflected shock wave were derived using a common iteration method based on one-dimensional shock tube theory [16].

The temperature dependencies of the ignition delay time (the induction time) are the key features of the mixtures investigated. OH radicals are the characteristic species indicating the hydrogen–oxygen and hydrocarbon–oxygen mixtures ignition. During the experiments, an excited OH* chemiluminescence signal was recorded by a Hamamatsu H9307-03 photomultiplier module equipped with an interference filter (310 ± 5 nm) to determine the ignition delay times. In combustible mixtures, the energy release in ignition is quite abrupt and leads to a dramatic increase in the OH concentration in both ground and excited states. Thus, a rapid rise in OH* chemiluminescence was considered as the end of induction time. The exact ignition moment was determined as the intersection of the inflectional tangent line of the OH* radiation intensity plot with the time axis. The increase in pressure was simultaneously recorded by a pressure gauge. The ignition development in hydrogen–oxygen mixtures was modeled using ChemKin
software package [17] by a recently suggested 20-reaction scheme for hydrogen combustion which describes that process well, particularly at low temperatures [18]. Figure 1 presents the measured and calculated ignition delay times in the reference mixtures of 6.7%H_2 + 3.3%O_2 + Ar and 13.3%H_2 + 6.6%O_2 + Ar at pressures of 2.2–2.7 bar. For modeling the pressure value P = 2.5 bar was used. The results show a good agreement.

3. Results
Unlike to other studied admixtures, trimethylphosphite (CH_3O)_3P being added to 13.3%H_2 + 6.6%O_2 + Ar mixture caused notable two-stage ignition development; typical signals of pressure and OH* radiation intensity are presented in figure 2. One can see the first gradual rise of OH* radiation and corresponding slow pressure increase at the time τ ≥ 200 µs (which one could call ‘pre-ignition’), and the secondary steep OH* radiation and pressure rise at τ ≥ 500 µs. While the ignition delay times measured by the steep rise of both signals in presence of 1%(CH_3O)_3P coincide with the measurements in the test mixtures, the pre-ignition occurs much earlier (figure 3). Trimethylphosphite thus certainly lack inhibiting activity in shock tube conditions. This result is not in contradiction with known flame-suppressant properties of phosphorus-containing species, as flame and shock tube kinetics differ significantly as was mentioned above.

Figures 4 and 5 summarize the temperature dependencies of the ignition delays measured in 6.7%H_2 + 3.3%O_2 + Ar and 13.3%H_2 + 6.6%O_2 + Ar mixtures doped by studied flame suppressants.

Recently developed kinetic mechanism of CCl_4 and CF_3H pyrolysis and oxidation [5] being used for modeling provided a good agreement of experimentally measured and calculated ignition delay times and allowed determining key reactions of influence of studied admixtures on hydrogen combustion. One should note that though radical-terminating reactions (1)–(3) dominated in CCl_4-doped mixture resulting in significant slowing of ignition, counteracting
Figure 3. The ignition and pre-ignition delay times observed in 1\%(\text{CH}_3\text{O})_3\text{P} + 13.3\%\text{H}_2 + 6.6\%\text{O}_2 + \text{Ar} mixture.

Figure 4. Experimentally observed (dots) and modeled (lines) ignition delay times in 6.7\%\text{H}_2 + 3.3\%\text{O}_2 + \text{Ar} mixture doped with various fire suppressants.

Figure 5. Experimentally observed (dots) and modeled (lines) ignition delay times in 13.3\%\text{H}_2 + 6.6\%\text{O}_2 + \text{Ar} mixture doped with various fire suppressants.

reaction \text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H} also plays quite an important role in combustion development. Thus, admixture pyrolysis which was previously shown to have dramatic influence on methane ignition [5] is significant even at temperatures below 1200 K.

According to NIST Chemical Kinetics Database many important reactions of C$_2$F$_4$Br$_2$, CF$_3$I and C$_3$F$_7$I pyrolysis and oxidation mechanisms are uninvestigated. The available data do not allow for reliable estimation of the numerous unknown rate constants, thus it is clear that the development of quantitative kinetic mechanisms describing hydrogen combustion inhibition requires new data on the kinetics of C$_2$F$_4$Br$_2$, CF$_3$I and C$_3$F$_7$I pyrolysis and oxidation. In particular, one could expect a great importance of pyrolysis reactions producing atomic bromine.
and iodine and consequent active radical formation in reactions \( \text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H} \) and 
\( \text{I} + \text{H}_2 \rightarrow \text{HI} + \text{H} \). Therefore an analysis of possible mechanisms of interaction of brominated and iodinated hydrocarbons with hydrogen–oxygen mixtures is the task for the future studies.

4. Conclusion

Influence of various halogenated and phosphorated inhibitors, namely \( \text{CCl}_4 \), \( \text{CF}_3\text{H} \), \( \text{C}_2\text{F}_4\text{Br}_2 \), 
(\( \text{CH}_3\text{O} \))\(_3\)\( \text{P} \), \( \text{CF}_3\text{I} \) and \( \text{C}_3\text{F}_7\text{I} \) on shock-induced ignition of hydrogen was experimentally investigated. Observed temperature dependencies of induction times indicate that \( \text{CF}_3\text{H} \) and (\( \text{CH}_3\text{O} \))\(_3\)\( \text{P} \) certainly lack inhibiting activity (well known for flames) at given shock wave conditions, while the effectiveness of halogen-containing specie dramatically increases in a row 
\( \text{Cl} \rightarrow \text{Br} \rightarrow \text{I} \). \( \text{C}_3\text{F}_7\text{I} \) provided an unique combination of combustion suppression and safety for human health and ecology.

Acknowledgments

This work has been supported by the Russian Science Foundation, grant No. 14-19-00025.

References

[1] Hastie J W 1973 J. Res. Natl. Bur. Stand., Sect. A 77 733–54
[2] Babushok V, Noto T, Burgess D R, Hamins A and Tsang W 1996 Combust. Flame 107 351–67
[3] Azatyan V V, Shebeko Yu N, Shebeko A Yu and Navtsevna Y Yu 2010 Russ. J. Phys. Chem. B 4 760–8
[4] Drakon A V, Eremin A V, Korobeinichev O P, Shvartsberg V M and Shmakov A G 2016 Combust., Explos. Shock Waves 52 375–85
[5] Drakon A, Eremin A, Matveeva N and Mikhailova E 2017 Combust. Flame 176 592–8
[6] Drakon A, Emelianov A and Eremin A 2014 Shock Waves 24 231–7
[7] Babushok V I, Linteris G T and Meier O C 2012 Combust. Flame 149 3569–75
[8] Azatyan V V and Saikova G P 2013 Russ. J. Phys. Chem. A 87 1615–21
[9] Alekseev V I, Elmenko A A, Zaretskij N P, Ponomarev N N, Chayakov B B, Chernykh E B 
and Shepetov N G 2011 Abstract of invention, Patent RU 2 485 164 C2
[10] Hastie J W and Bonnell D W 1980 Molecular chemistry of inhibited combustion systems Report NBSIR 80-2169 (Washington, DC: Nat. Bur. Stand.)
[11] Korobeinichev O P, Shvartsberg V M, Shmakov A G, Bolshova T A, Jayaweera T M, Melius C F, Pitz W J and Westbrook C K 2004 Proc. Combust. Inst. 30 2353–60
[12] Korobeinichev O P, Shvartsberg V M, Shmakov A G, Kniazev D A and Rybitskaya I V 2007 Proc. Combust. Inst. 31 2741–8
[13] Jayaweera T M, Melius C F, Pitz W J, Westbrook C K, Korobeinichev O P, Shvartsberg V M, Shmakov A G and Curran H 2005 Combust. Flame 140 103–15
[14] Shvartsberg V M, Shmakov A G, Bolshova T A and Korobeinichev O P 2012 Energy Fuels 26 5528–36
[15] Korobeinichev O P, Rybitskaya I V, Shmakov A G, Chernov A A, Bolshova T A and Shvartsberg V M 2009 Proc. Combust. Inst. 32 2591–7
[16] Gaydon A G and Hurle I R 1963 The Shock Tube in High Temperature Chemical Physics (London: Verlag Chapman and Hall Ltd.)
[17] Kee R J, Rupley F M and Miller J A 1993 CHEMKIN-II: A FORTRAN chemical kinetics package for the analysis of gas-phase chemical kinetics Report SAND89-8009B (Albuquerque, NM: Sandia National Laboratories)
[18] Hong Z, Davidson D F and Hanson R K 2011 Combust. Flame 158 633–44