STUDY OF FIRE SUPPRESSION EFFECTIVENESS OF ORGANOPHOSPHORUS COMPOUNDS AND COMPOSITIONS ON THEIR BASE

Oleg P. Korobeinichev, Andrey G. Shmakov,
Vladimir M. Shvartsberg, Sergey. A. Yakimov
Institute of Chemical Kinetics & Combustion,
Novosibirsk, 630090 Russia
Phone: +7-3833-332852;
Fax: +7-3833-307350
E-mail: korobein@kinetics.nsc.ru

ABSTRACT

The cup-burner technique was used to continue study of the effectiveness of recently synthesized organophosphorus (OPCs), organofluoric compounds (OFCs) and aqueous solutions of some organic salts. The composite fire suppressants - mixtures of earlier studied OPCs with other compounds including halons, organic salts of alkali metals were tested. The dependence of suppression effectiveness of n-heptane/air flame on ratio of the components in the blend was studied. The perspectives of practical application of the tested fire suppressants for fire-fighting are discussed.

INTRODUCTION

Search and study of novel effective and ecologically safe fire suppressants is one of a perspective direction of investigation in area of fire suppression. In this connection organophosphorus (OPCs), organofluoric (OFCs) and metal-containing compounds (MCCs) is study of a great interest. At present the results of comparative testing of various flame suppressants are available [1-10] but there is a deficit in experimental data on minimal extinguishing concentration (MEC) for many compounds and especially for composite fire suppressants. The MEC is necessary for evaluating of perspectives of practical application of the compounds. The search and testing of novel fire suppressants - halons alternatives among OPCs, OFCs and MCCs still presents a perspective direction of investigation. High boiling point (low volatility) of studied OPCs brought us to synthesis of more volatile fluorinated derivatives of OPCs. However a high reactivity of some of fluorinated OPCs, which were recently synthesized [1-5], hinders their practical use. Nevertheless, the application of moderately volatile OPCs as fire suppressants is quite possible using blends of OPCs with ozone-friendly halons as a potential delivery media.

At present some data on effectiveness of flame inhibition and extinguishing by various OPCs in laboratory conditions were published in [6-10]. However in the literature there are no data on the extinguishing concentrations of blends of OPCs with another compounds. The efficiency of such blends can be higher than sum of efficiency of individual components. The goal of present work is to determine the effectiveness of OPCs, OFCs, MCCs and their blends with ozone-friendly halons in laboratory tests.

EXPERIMENTAL

In the present paper we studied novel OPCs and OFCs. Their formulas and boiling points are presented in Table 1. In Table 1 earlier investigated OPCs and halons, which we used as components of blends, are also given. In addition we studied the effectiveness of inorganic and organic salts (K_3PO_4, $KOOCH_3$, KOOCCOOK and $K_4[Fe(CN)_6]$) in form of fine aerosol using cup-burner technique. The scheme of experimental setup is presented in Figure 1.

Table 1. Novel OPCs and OFCs tested and their boiling points

Formula	B.P. at atm. pressure
$[(CF_3)_2CHO]_2P(O)CH_3$	180
$[(CF_3)_2CHO]_2P(O)CF_3$	135
$(CH_3O)P(O)CF_3(CH_3)$	150
$(CF_3CH_2O)_3P$	131
$HCF_2CF_2CH_2OCF_2CHFCF_3$	80
$HCF_2CF_2OCH_2CH_3$	82
$CF_3CF_2CF_2OCHFCF_3$	70
$(CF_3)_2C{=}CFCF_2CF_3$	42
$(CF_3)_2CFCF{=}CFCF_3$	45
CF_3H	-82.2
C_2F_5H	-48.6

The detail of cup-burner technique was described in our previous work [3]. The salts were introduced into the airflow in form of aqueous solutions using a nebulizer. The mass-median diameter of the aerosol droplets was about 10-20 microns whereas after evaporation of water the size of particles became 2.5 - 5 microns. The deposition of the salts inside the chimney was taken into account. The contribution of water from the solutions into the inhibition effect was also taken into account. Besides we studied blends of OPCs with organic salts of alkali metals, ozone-friendly halons (CF_3H, C_2F_5H).

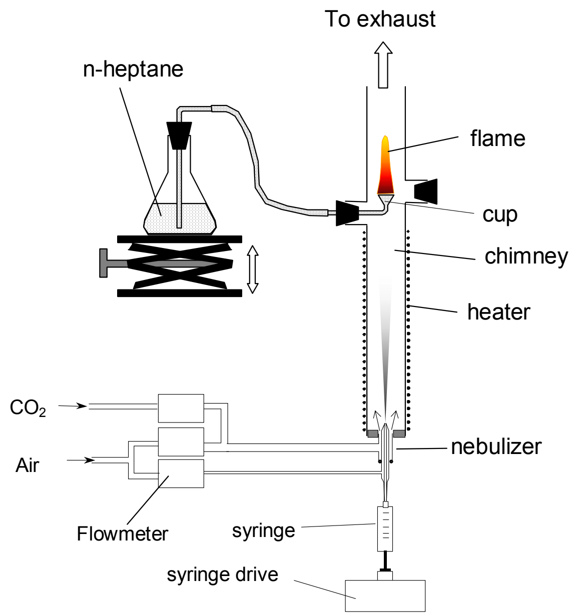

Fig. 1. Cup-burner setup.

RESULTS AND DISCUSSION

Cup-burner tests

A number of novel OPCs, OFCs and MCCs were tested using the cup-burner technique. The extinguishing concentration of CO_2 as a function of the dopant loading is shown in Figure 2. The measured extinguishing concentrations for the tested compounds are tabulated below (Table 2). For some compounds a secondary flame in upper part of the chimney was observed because of combustion of their vapours in heated airflow. For these OPCs and OFCs a distinctive dependence of CO_2 extinguishing concentration on suppressants loading is observed (see Fig. 2). For example, when suppressants loading increases a higher concentration of CO_2 is required for flame extinguishing. This effect as it was reported by us earlier [3] is connected with 2 competitive processes: (1) the flame inhibition by suppressants and temperature decrease; (2) an increase of flame temperature due to additional heat release from suppressants combustion that decreases its effectiveness as fire suppressant.

Table 2. Extinguishing concentrations of novel OPCs and OFCs at 75 ^{0}C.

Compound	Minimal extinguishing concentration,		air stability
	% by volume	g/m^3	
$(CF_3CH_2O)_3P$	2.6±0.2	381	No fumes
$[(CF_3)_2CHO]_2P(O)CH_3$	3.0±0.2	530	No fumes
$[(CF_3)_2CHO]_2P(O)CF_3$	2.0±0.2	400	No fumes
$HCF_2CF_2CH_2OCF_2CHFCF_3$	6.1±0.3	768	No fumes
$HCF_2CF_2OCH_2CH_3$	flammable	-	No fumes
$CF_3CF_2CF_2OCHFCF_3$	6.6±0.3	843	No fumes
$(CF_3)_2C{=}CFCF_2CF_3$	4.8±0.3	642	No fumes
$(CF_3)_2CFCF{=}CFCF_3$	5.0±0.3	670	No fumes
CF_3Br	4.6	306	-
CF_3H	14.2	443	-
C_2F_5H	11.4	610	-

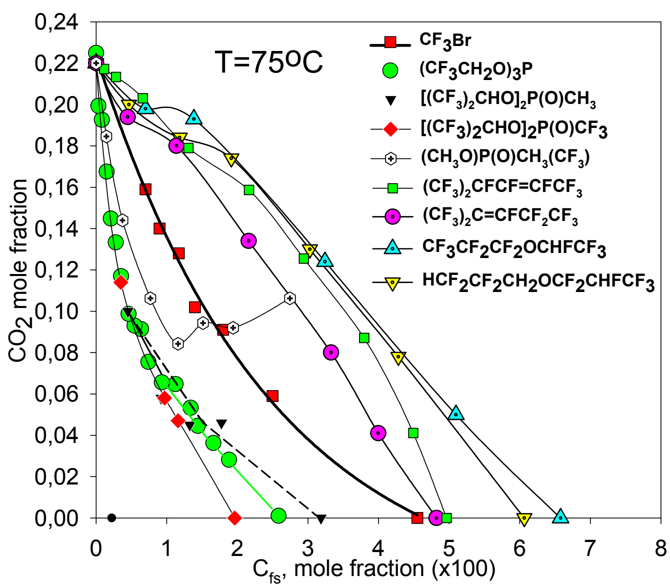

Figure 2. Cup burner tests: extinguishing concentration of CO_2 as a function of loading of fire

Thus, a different effectiveness of various suppressants can be explained by influence of several reasons: chemical mechanisms of suppression, the heat of formation of suppressants, heat capacity of their vapours, their destruction rate and destruction products in a flame. The results presented in Table 2 and Figure 2 indicate that under the same conditions the effectiveness of some OPCs is higher than that of CF_3Br in 1.8 - 2.3 times. In this case the relative effectiveness is the ratio of minimal extinguishing concentrations. The most effective OPC in this test is $[(CF_3)_2CHO]_2P(O)CF_3$. Among the OFCs the most effective are

$(CF_3)_2C=CFCF_2CF_3$ and $(CF_3)_2CFCF=CFCF_3$. Probably high efficiency of this compound can be explained by presence of double bonds in their molecules. The double bounds can be additional traps for radicals H and OH in a flame. As have shown in experiments the location of double bounds in the molecule does not influence on efficiency of these suppressants. The basic determining factor for suppression effectiveness in these compounds was shown to be the high degree of replacement of hydrogen atoms for fluorine.

The results on extinguishing of diffusive cup-burner flame (*n*-heptane + air) by aqueous solutions of various salts are presented in Table 3. The values of MEC obviously demonstrate potassium salts to be on order of magnitude more effective fire suppressants than OPCs and halons [9]. The data obtained indicate that the suppression effectiveness counting on one molecule of organic salts is actually proportional to number of potassium atoms (the effect of water being taking into account). This rule is not correct for $K_4[Fe(CN)_6]$ containing iron atoms except potassium ones. Iron-containing compounds are known to be one of the most effective inhibitors of combustion [9]. In the case of $K_4[Fe(CN)_6]$ iron and potassium act reciprocally suppressing the flame. The results obtained do not show synergy of iron and potassium. Further search of synergy of iron and potassium salts will be an objective of future research.

It is noteworthy that a combined application of phosphorus and potassium (as solution of potassium phosphates KH_2PO_4 or $KOOCH_3$ with OPCs additive) for flame suppression is as effective as inert agent. The suppression effectiveness of the composition is very low, so we failed to extinguish the cup-burner flame. Nevertheless earlier [5] we demonstrated that $NH_4H_2PO_4$ and OPCs at loading of 0.2% by volume demonstrate nearly the same effectiveness of suppression counting on one atom of phosphorus. Thus the expected effectiveness of K_3PO_4 must be much higher than that for OPCs but it is not confirmed experimentally. Thermally stable potassium phosphate (K_3PO_4) does not dissociate effectively producing chemically active species of potassium and phosphorus oxy-acids. To understand the detailed mechanism of mutual decrease of effectiveness K- and P-containing inhibitors additional research is required. Thus the practical application of such combined fire suppressants has no perspectives.

Table 3. The studied salts and their minimal extinguishing concentration

Salt	minimal extinguishing concentration	
	mole fraction (×100)	g/m^3
K_3PO_4	No extinguishing at 1%	
$KOOCH_3$	0.25	10.9
KOOCCOOK	0.13	9.6
$K_4[Fe(CN)_6]$	0.035	6.6

The efficiency of blends OPCs and organic salts of alkali metals with C_2F_5H was determined using cup-burner method. OPCs or aqueous solutions of the salts were introduced in into the airflow using a nebulizer. The C_2F_5H flow was added to the airflow in discrete steps so to reach flame extinguishment. The results obtained are presented in Fig. 3 and Fig 4

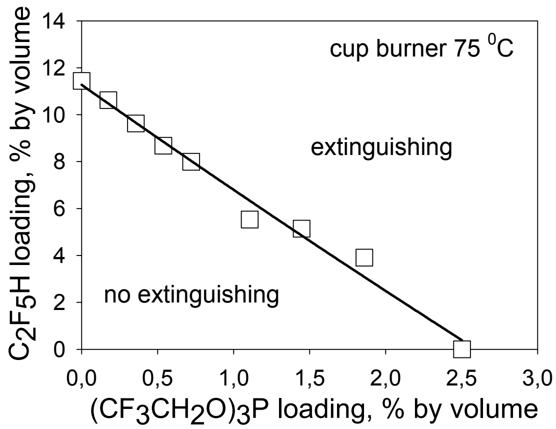

Figure 3. Cup burner tests: extinguishing concentration of C_2F_5H as a function of loading of $(CF_3CH_2O)_3P$.

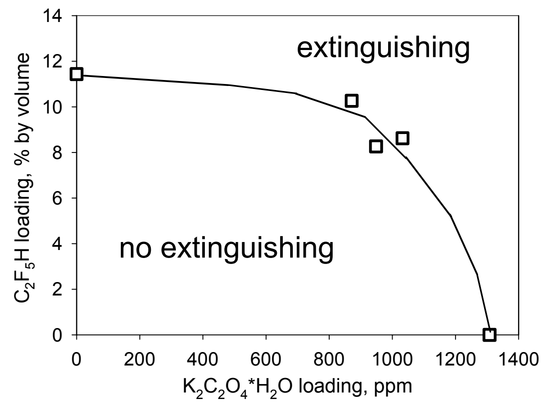

Figure 4. Cup burner tests: extinguishing concentration of C_2F_5H as a function of loading of $K_2C_2O_4 \cdot H_2O$.

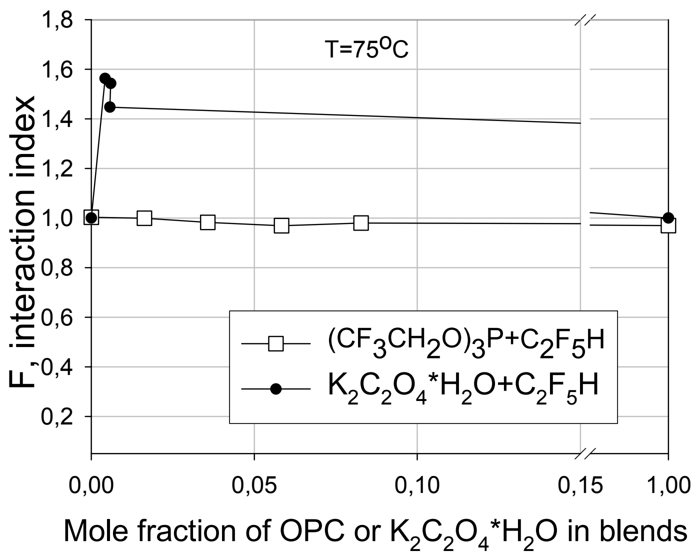

Figure 5. Interaction index for blends of $CF_3CH_2O)_3P$ or $K_2C_2O_4$*H_2O with C_2F_5H

For the studied blends the parameter F (index of interaction) was calculated according the formula proposed in Ref [11]:

$$F = \frac{C^{fs}}{C_0^{fs}} + \frac{C^D}{C_0^D}$$

where C_0^{fs} and C^{fs} - minimal extinguishing concentration of OPC or $K_2C_2O_4 \cdot H_2O$ without C_2F_5H and in blends, C_0^D and C^D - minimal extinguishing concentration for pure C_2F_5H and in blends with OPC or $K_2C_2O_4 \cdot H_2O$. The received dependencies for blends of C_2F_5H with OPC or $K_2C_2O_4 \cdot H_2O$ are presented in Figure 5. As was shown earlier [11] the value of index of interaction reflects mutual influence of components of blend. According [11] if F > 1 such blend produce antisynergetic effect on extinguishing ability of the blend. At F=1 components influence reciprocally demonstrating no synergy. At F < 1 synergy is observed. It was revealed that the blends of the organic salts doped with C_2F_5H or OPCs have lower efficiency in comparison with individual compounds, i.e. such blends are not effective. We assume that such low effectiveness of the studied blends are connected with deactivation of active compounds – radical scavengers formed in a flame (oxides of phosphorus, oxide of alkaline metals) due to interaction with other flame species (e.g. HF in a case C_2F_5H). As a result inactive compounds are formed (KF, K_3PO_4 etc.). It was found that the efficiency of blends of OPCs with C_2F_5H equal the sum of efficiencies of individual components. Thus essential advantages of blends based on halons with OPC or with $K_2C_2O_4 \cdot H_2O$ have no prospective of practical application.

CONCLUSIONS

Thus, as a result of carried out study new OPCs, OFCs, and also organic salts of alkaline metals as well as a number of blends were investigated. Minimal extinguishing concentration of these compounds and blends were measured using cup-burner technique. The interaction index for components of the blends was determined. We showed that the blends of OPC and halons as well as organic salts of alkaline metals with halons demonstrate no synergy. The received data allows on the base of fluorinated noncombustible OPC to create new fire suppressants, which have high efficiency, wide working temperature range, low toxicity and cost.

ACKNOWLEDGEMENTS

This work was supported by the INTAS under Grant № 03-51-4724. The authors thank G.G. Furin for preparing the organofluoric compounds, V.K. Brel, E.E. Nifantev, I.Y. Kudryavtsev, E.I. Goryunov for preparing the organophosphorus compounds for our tests.

REFERENCES

1. Gann, R.G. "Next Generation Fire Suppression Technology Program: FY2003 Progress", *Halon Options Technical Working Conference*, Albuquerque, NM, NIST SP 984-1 (CD), (2003), http://www.bfrl.nist.gov/866/HOTWC/HOTWC2003/pubs/R0301557.pdf.

2. Mather, J.D., Tapscott, R.E., Shreeve, J.M., Singh, R.P., *Halon Options Technical Working Conference*, Albuquerque, NM, NIST SP 984-1 (CD), (2003), http://www.bfrl.nist.gov/866/HOTWC/HOTWC2003/pubs/R0301564.pdf.

3. Korobeinichev, O.P., Shmakov, A.G., Shvartsberg, V.M., Knyazkov, D.A., Makarov, V.I., Koutsenogii, K.P., Samsonov, Yu.N., Nifantev, E.E., Kudryavtsev I,Y., Goryunov, E.I., Nikolin, V.P., Kaledin,V.I., *Halon Options Technical Working Conference,* Albuquerque, NM, NIST SP 984-1 (CD), (2003), http://www.bfrl.nist.gov/866/HOTWC/HOTWC2003/pubs/R0301562.pdf.

4. Shmakov A.G., Korobeinichev O.P., Shvartsberg V.M., Knyazkov D.A., Bolshova T.A. and Rybitskaya I.V., *Proceedings of the Combustion Institute,* 30, #2, pp.2345-2352 (2004).

5. Korobeinichev, O. P.; Shmakov, A. G.; Chernov, A. A.; Shvartsberg, V. M.; Rybitskaya, I. V.; Makarov, V. I.; Nifantev, E. E.; Kudryavtsev, I. Y.; Goryunov, E. I.; *Halon Options Technical Working Conferences*, Albuquerque, NM, NIST SP 984-2 (CD), (2004). http://www.bfrl.nist.gov/866/HOTWC/HOTWC2004/pubs/R0401176.pdf.

6. Riches, J., Grant, K., and Knutsen, L., *Halon Options Technical Working Conference*, Albuquerque, NM, (1999), pp. 444-452. http://www.bfrl.nist.gov/866/HOTWC/HOTWC2003/pubs/R9902743.pdf.

7. Knutsen, L, Morrey, E. and Riches J., *Halon Options Technical Working Conference, Albuquerque,* NM, (2001), pp. 235-240 http://www.bfrl.nist.gov/866/HOTWC/HOTWC2003/pubs/R0200493.pdf.

8. Morrey, E., Knutsen, L., *Halon Options Technical Working Conference*, Albuquerque, NM, NIST SP 984-1 (CD), (2003), http://www.bfrl.nist.gov/866/HOTWC/HOTWC2003/pubs/R0301565.pdf.

9. Linteris, G.T., *Halon Options Technical Working Conference*, Albuquerque, NM, (2001), pp.187-197. http://www.bfrl.nist.gov/866/HOTWC/HOTWC2003/pubs/R0200488.pdf.

10. Linteris, G.T., Katta V.R. Takahashi F., Combust. Flame 138 (2004) 78-96.

11. Lon J.L. and al. Fire Technology, Third Quarter. – 1996.- pp.260-271.