

# On the mechanism of action of phosphorus-containing retardants

Andrey G. Shmakov,<sup>a</sup> Vladimir M. Shvartsberg,<sup>a</sup> Oleg P. Korobeinichev,<sup>\*a</sup>  
Mark W. Beach,<sup>b</sup> Terry I. Hu<sup>b</sup> and Ted A. Morgan<sup>b</sup>

<sup>a</sup> Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences,  
630090 Novosibirsk, Russian Federation. Fax: +7 383 330 7350; e-mail: korobein@kinetics.nsc.ru

<sup>b</sup> The Dow Chemical Company, MI 48667, Midland, USA. Fax: +1 989 638 6686; e-mail: MWBeach@dow.com

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An additive of triphenylphosphine oxide (Ph<sub>3</sub>PO), which is a widely used flame retardant, was shown to inhibit a CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> flame by decreasing concentration of active flame species H and OH.

Polymeric materials offer many advantages over the other classes of materials and are used in many commercial applications. However, the majority of commercial organic polymers have a serious shortcoming – flammability. The flammability of these polymer materials is reduced by the addition of chemically active compounds, which are flame retardants. These retardants reduce the base polymer's flammability by either condensed and/or in gas-phase mechanisms. A study of the chemical flame structure of a burning polymer doped with a flame retardant could help to understand the fundamental mechanism of the flame retardant's action. Such a study should also allow determination of the type of gas phase activity, which could be thermophysical and/or chemical (inhibition of chain reactions) in nature. One hypothesis for the active gas-phase mechanism for flame retardants is by chain termination reactions that involve the interaction of retardants or their degradation products with active flame species, mainly H and OH radicals. According to this hypothesis, a retardant additive reduces H and OH concentration in the gas-phase flame and serves as an effective scavenger of H and OH radicals.

To determine the gas-phase mechanism for a flame retardant additive, the chemical structure of a CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> flame without and with a flame retardant additive was measured using molecular beam mass spectrometry (MBMS). MBMS with soft ionization<sup>1</sup> allows measurement of the concentration of most labile flame species, which includes both atoms and free radicals. The study of flame retardants in a flame without added polymer is a simplified approach as it neglects the polymer and possible polymer–flame retardant interactions. Nevertheless, such simplified studies allow an assessment of whether certain flame retardants can provide gas-phase activity and the type of chemical interactions that may be involved in the gas phase.

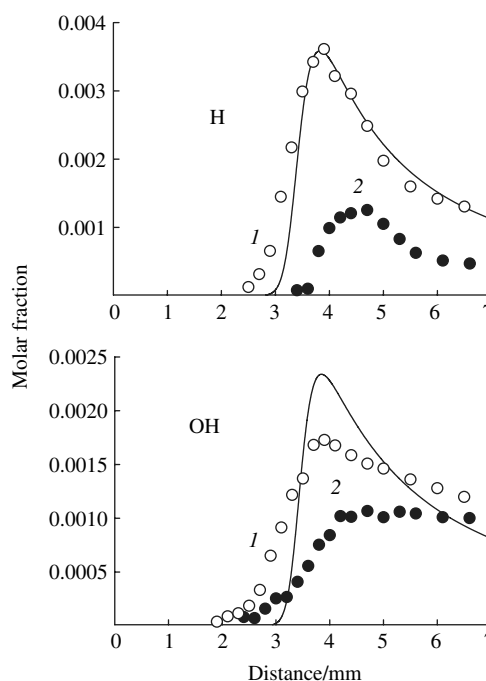
For flame studies with flame retardants, a stabilized Bunsen-type burner was used under near-adiabatic conditions. The choice of the basic Bunsen flame is justified by a number of factors. Bunsen flames minimize heat loss (unlike flat burner-stabilized flames), which facilitates a comparison of measured and simulated flame structures. Bunsen flames also lack a porous plate, which is common to a flat burner configuration. The lack of a porous plate does not prevent the direct feeding of solids into unburnt gases in the flame. However, it minimizes chain termination on the burner surface, which commonly occurs with a flat burner flame configuration.

McBee and Hastie<sup>2</sup> performed a qualitative spectroscopic and mass-spectroscopic study of the structure of flames stabilized on a Bunsen burner at atmospheric pressure. The cited work

involved the addition of triphenylphosphine oxide but did not involve calibrations so absolute concentrations of flame species were not determined.

The goal of this study was to establish the mechanism of action of phosphorus-containing retardant and to determine its influence on H and OH concentration directly in a flame environment.

The structure of premixed CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> (0.0918/0.1554/0.7528) flame stabilized on Mache-Hebra nozzle burner<sup>3</sup> (a type of Bunsen burner with constricted nozzle providing a uniform distribution of gas velocity) was determined at atmospheric pressure without additives and doped with 0.0190±0.001 vol% triphenylphosphine oxide (TPPO) Ph<sub>3</sub>PO. The composition of the combustible mixture was chosen such that the flame temperature was below 1700 °C. This makes possible the use of a quartz probe for probing the flame. The TPPO loading was chosen to decrease the flame speed by not more than in 1.5 times. TPPO feeding into unburnt gases was *via* a specially designed two-sectional evaporator, which was placed inside the burner.



**Figure 1** Profiles of concentration of H and OH in CH<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> flame (1) without additive and (2) doped with 0.0190 vol% TPPO. Circles – experiment, lines – modeling data (for undoped flame only).

The fused TPPO with a certain velocity was pressed by the piston from the first section of the evaporator with  $T = 180\text{ }^{\circ}\text{C}$  to the second section with  $T = 300\text{ }^{\circ}\text{C}$ , where it evaporated. The final TPPO loading was determined by taking into account actual losses inside the burner.

Profiles of concentration of flame species were measured using MBMS with soft electron-impact ionization. The experimental setup used in the MBMS study was described previously.<sup>1</sup> A quartz cone with an orifice diameter of 0.08 mm, a wall thickness of about 0.05 mm, and an internal angle at the apex of  $40^{\circ}$  was used as the probe. In this case, the burner was inclined at an angle of about  $45^{\circ}$  to the vertical so that the probe axis was perpendicular to the flame front. A quadrupole mass spectrometer with an upgraded ion source and soft electron-impact ionization with a small spread of electron energy was used to measure the mass spectra of the gases sampled from the flame. The intensities of peaks at  $m/z$  1 (H) and 17 (OH) were measured at an ionizing energy of 16.2 eV, which is low enough in energy to prevent fragmentation. The calibration coefficients for H and OH were determined by comparing their corresponding peak intensities in the post-flame zone and calculated H and OH concentration assuming partial equilibrium of the three most 'rapid' reactions ( $\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$ ;  $\text{H}_2 + \text{O} = \text{H} + \text{OH}$ ;  $\text{O}_2 + \text{H} = \text{OH} + \text{O}$ ).<sup>4</sup> The relative error of measurement intensities of peaks corresponding to the active species was  $\pm 40\%$ .

The structure of the flame without retardants was simulated using PREMIX and CHEMKIN codes (SANDIA National Laboratories, USA) and the kinetic mechanism for the hydrocarbon oxidation [77 species (H, O, C, N) and 469 reactions].<sup>5,6</sup> This mechanism is available at a web site.<sup>7</sup>

The introduction of the flame retardant additive into the flame slightly decreases the final flame temperature (for  $\approx 110\text{ K}$ ) and increases the width of the combustion zone by about 60–70%. There are two factors that may be responsible for the temperature drop: (1) thermophysical, *i.e.* dilution of the combustible mixture as a result of adding TPPO to the rich flame and (2) a decrease of completeness of combustion as a result of deceleration of methane oxidation. The addition of methane into the flame in an amount equivalent to carbon content in the TPPO additive reduced the final temperature of the flame only for 20 K. Thus, the decrease temperature observed after addition of TPPO is beyond that occurs from a purely thermophysical effect.

In Figure 1, the measured and simulated concentration profiles of H and OH in the pure and TPPO-doped flames are shown. Figure 1 demonstrates that the additive decreases both maximal (in about 2.8 times) and post-flame (in about 2.6 times) concentrations of H atoms. The TPPO additive noticeably decreased OH concentration in the flame as well: maximal concentration dropped about 1.7 times, whereas post-flame concentration decreased by only about 10%. Therefore, the effectiveness of an inhibitor for gas-phase activity can be estimated by the decrease of concentration of radicals in the reaction zone of a flame, *i.e.*, by maximal concentration.

Data were obtained to estimate the contribution of thermo-physical (temperature decrease) and chemical (chain termination in reactions with the inhibitor) factors that contributed to the

total drop of H and OH concentrations observed in TPPO flame measurements. Modeling calculations predicted that an addition of about 7 vol% inert  $\text{N}_2$  into the flame should drop the post-flame temperature by about 110 K and decrease the maximal H concentration by about 37%. Thus, the decrease in H concentration caused by the TPPO additive was about five times more than the overall effect predicted from calculations. Though under these conditions (fuel to oxidizer ratio 1.2), the effectiveness of a retardant can be evaluated by a decrease of maximal (in reaction zone) H concentration in the flame. These measurements agree with the previous temperature measurements, that the flame changes observed are chemical and not a thermo-physical effect.

The effect of TPPO on the flame speed was measured using the method of total area of the flame cone.<sup>2</sup> Relative error of the method was about  $\pm 5\%$ . The addition of 0.0190 vol% TPPO caused a drop in burning velocity of the flame of about 30%. This result is an agreement with the decrease in H and OH concentrations in the flame after addition of TPPO as measured by MBMS. It also confirms the use of the MBMS technique as a tool to determine the relative effectiveness of flame retardants in flames.

These studies show that TPPO affects the flame as an effective inhibitor: its addition to the flame appreciably decreased both the burning velocity and the concentration of active species in the reaction zone of the flame. At the same time, the TPPO additive produced a negligible thermal effect on the flame.

These studies point to TPPO as potential effective gas-phase flame retardant for a polymer blend. This neglects any possible polymer-flame retardant interactions. It is also important to consider the delivery and degradation of the flame retardant relative to the polymer. Nevertheless, these studies confirm the use of MBMS as fundamental probe for possible gas-phase flame retardant activity.

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