Kinetics and mechanism of thermal decomposition of triphenyl phosphate in flow reactor

Shamkov Andrey G.,[1*] Mebel Alexander M.,[2] Korobeinichev Oleg P.,[1] Porfiriev Denis P.,[3] Osipova Ksenia N.,[1] Gerasimov Ilya E.,[1] Knyazkov Denis A.,[1] Yang Bin[4]

[1] *Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, Institutskaya 3, 630090, Novosibirsk, Russia*

[2] *Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, 33199, Miami, Florida, USA*

[3] *Samara National Research University, Moskovskoye shosse 34, 443086, Samara, Russia*

[4] *Tsinghua University, Tsinghua Yuan No.1, Haidian District, 100084, Beijing, China*

** E-mail: shmakov@kinetics.nsc.ru*

The main method for reducing the combustibility of polymeric materials is the introduction of flame retardants into them. An important scientific problem is understanding the mechanism of action of a flame retardant during the combustion of a polymer. The purpose of this work was to experimentally and theoretically study the conversion of triphenyl phosphate (TPP) during its thermal decomposition in an inert medium, i.e. under conditions that are characteristic of the flame zone near the surface of the polymer.

The high-temperature pyrolysis of TPP vapor in Ar was studied by using thermal flow reactor at a pressure of 1 atm. Mass spectra of products of thermal decomposition of TPP vapors were measured by probe molecular beam mass spectrometry at 300-1000°C. Using the G3(MP2,CC) model chemistry along with the B3LYP method in the framework of density functional theory (DFT) with the 6-311G(d,p) basis set, calculations were performed to optimize the geometry of all structures on the considered potential energy surfaces of TPP and products of primary and secondary decomposition of TPP. The kinetic rate constants of the thermal decomposition reaction of TPP were also calculated using the RRKM theory and the method of the main kinetic equation (RRKM-ME) implemented in the MESS program code, thermochemical parameters for TPP and products of primary and secondary decomposition of TPP in temperature range 200-6000K were obtained. Based on the results of calculations, as well as the mechanisms of transformation of the phenyl and phenoxyl radicals from the literature, a combined detailed chemical-kinetic mechanism was created that describes the pyrolysis of TPP in inert medium.

Comparison of the results of numerical calculations of the composition of TPP pyrolysis products in the reactor showed that the developed mechanism quantitatively predicts the dependence of the TPP concentration on the reactor temperature distribution, and for intermediate compounds this mechanism well describes the experimentally observed trends in the conversion of phosphorus-containing substances on the reactor temperature.

This work is supported by the Russian Foundation for Basic Research (Project №21-53-53026).