

Experimental and theoretical study of the kinetics and mechanism of thermal decomposition of triphenyl phosphate in inert media

Andrey Shmakov¹, Alexander Mebel², Oleg Korobeinichev¹, Denis Porfiriev³,
Ksenia Osipova¹, Ilya Gerasimov¹, Denis Knyazkov¹, Bin Yang⁴

¹ Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, 3, Institutskaya str.,
Novosibirsk, Russia, 630090

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

³ Samara National Research University, 34, Moskovskoye shosse, Samara, Russia, 443086

⁴ Tsinghua University, Tsinghua Yuan No.1, Haidian District, Beijing, China, 100084
shmakov@kinetics.nsc.ru

The increasing use of synthetic polymer materials has in many cases been held back by their high fire hazard. The reducing the flammability of polymers is one of the most important problems. The main method for reducing the combustibility of polymeric materials is the introduction of flame retardants into them. One of the well-established classes of flame retardants are organophosphorus compounds. However, until now, scientists still do not know how processes involving phosphorus-containing flame retardants occur in real objects. The main scientific issue is the site of action of flame retardants, since they can both slow down the thermal decomposition of polymers and reduce the rate of release of combustible gases from them, as well as suppress the combustion of these combustible gases when mixed with ambient air. It is also important to understand how the chemical structure of flame retardant molecules affects the above two processes, since such information can help to purposefully synthesize flame retardant molecules with the desired structure. Thus, 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 argon 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 in the temperature range of 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 Rice-Ramsberger-Kassel-Marcus 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 phenoxy 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)