Tri phenyl phosphate decomposition through the reaction with H, CH_3, OH radicals

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Tri phenyl phosphate $C_{18}H_{15}O_4P$ (TPP) is widely used as flame retardant during polymer combustion processes. From 10% to 20% of TPP addition results in reduction of the flame spread rate, the mass burning rate and conductive heat flux from the flame to the polymer surface. Hence, the study of TPP interaction with widespread radicals like H, CH_3, OH in the combustion conditions and subsequently decomposition of TPP are essentials for the further reducing of polymer flammability.

The geometries and vibrational frequencies of tri phenyl phosphate and its decomposition products are calculated using the methods of density functional theory, using the functional ωB97XD[1,2].

The proposed ways of TPP decomposition are as follows – 1) addition of H atom in TPP structure leads either to H2 migration from one of C_6H_5O moiety or to addition of H atom on C1 atom of C_6H_5O, which both then lead to C-O cleavage and $C_{12}H_{10}O_4P$ compound. 2) addition of OH and subsequent decomposition on $C_{12}H_{10}O_4P$ and C_6H_5OH and as well 3) addition of CH_3, which will finally form $C_{12}H_{10}O_4P$ and C_7H_8. Then, $C_{12}H_{10}O_4P$ will undergo the series of C-O and P-O cleavages and be decomposed.

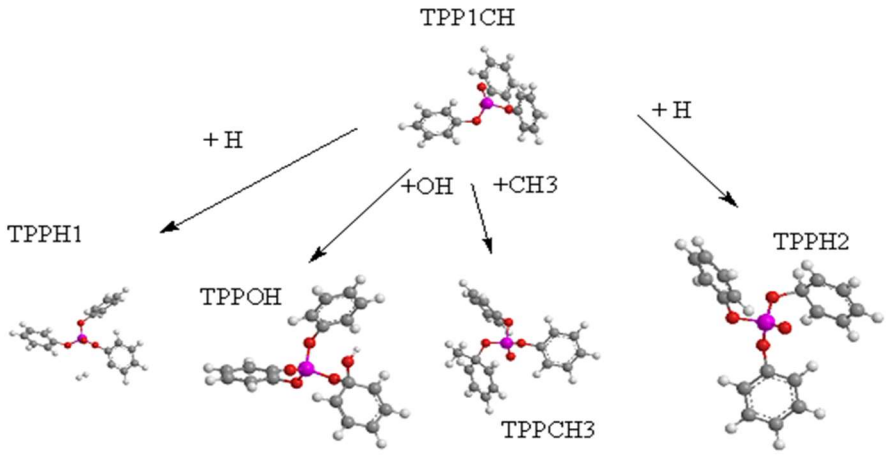

Fig.1 – The proposed initial pathways steps for $C_{18}H_{15}O_4P$ + H/OH/CH_3

In the work the probable pathways have been predicted and as well the potential energy surface (PES) has been presented. PESs were optimized at the density functional ωB97XD/6-31G* level of theory. This reaction is explored by the means of DFT theory and couple-cluster technique combination, realized with Gaussian 09 and MOLPRO 2020 software. Electronic structure/Rice-Ramsperger-Kassel-Marcus Master Equation calculations were applied to unravel the mechanism and kinetics of the $C_{18}H_{15}O_4P$ + H/OH/CH_3. All the gained values of reaction compounds energies and frequencies have been used to calculate pressure and temperature dependent reaction rate constants and product branching ratios.

References

1. J.-D. Chai, M. Head-Gordon, *J. Chem. Phys.* **2008**, 128, 084106.
2. J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, 10, 6615 (2008).