

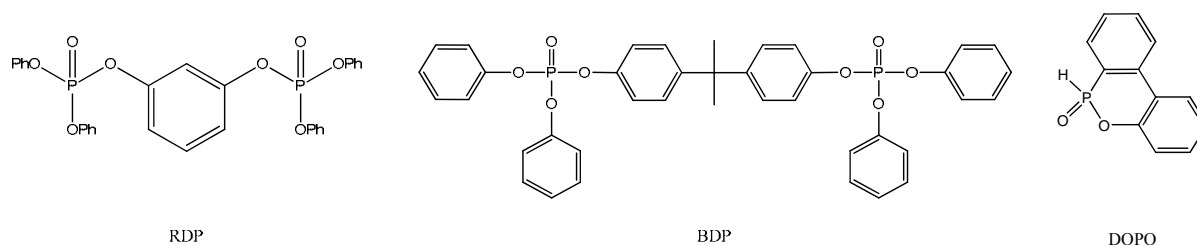
CHARACTERIZING TECHNICAL MIXTURES OF RDP, BDP, AND DOPO USING MULTIPLE ANALYTICAL TECHNIQUES

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Introduction

Halogenated flame retardants (HFRs) have been widely incorporated into polymeric material due to their perceived effectiveness, affordability, and low impact on the characteristics of the treated polymer. However increased scientific research on HFRs has led to a heightened concern regarding their fate in the environment as well as their potential health effects. Indeed, existing and emerging regulations are forcing industry to look for alternative halogen-free flame retardants (HFFRs) for use in a growing number of polymer based consumer products and, as such, phosphorus-based flame retardants are receiving notable attention in Europe and East Asia.¹ Due to the wide range of applications that polymers are utilized for, their formulations tend to be application specific with each formulation consisting of different resins, hardeners, and fire retardants. The mechanisms by which phosphorus flame retardants (PFRs) act is not straightforward since the degradation of any specific polymer during a fire would be strongly dependent on the other components present. It has been suggested that PFRs can be effective in the gas phase and by facilitating charring.² PFRs can be incorporated into polymers through blending (as additive flame retardants) or via chemical reactions (as reactive flame retardants)². Additive PFRs are commonly used in combination with each other and triphenyl phosphate (TPP) to increase their overall effectiveness while reducing the required loading¹, but little is known about the environmental fate of these compounds³. This is further complicated by the fact that the information available on the composition of PFR technical products is open-ended – for instance, technical BDP is listed by a supplier as having a phosphorus content of > 8.8%.⁴ In this work, we investigated the isomeric composition of two common additive PFRs, Resorcinol bis(diphenyl phosphate) (RDP) and Bisphenol A bis(diphenyl phosphate) (BDP), as well as a reactive OPFR, 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO).



Materials and methods

Samples of RDP, BDP, and DOPO were provided by Susanne L. Waaijers (IBED, University of Amsterdam) and were characterized through a combination of LC/UV, LC/MS/MS, GC/MS, NMR (¹H and ³¹P NMR), and preparatory thin-layer chromatography (prep-TLC) experiments. LC/UV experiments were conducted using a Waters Prep LC 4000 System coupled to a Waters 2487 Dual λ Absorbance detector using a μ Bondapak C18 column (10 μ m, 3.9 x 300 mm). LC/MS/MS experiments were conducted on a Waters Acquity UPLC coupled to a Micromass Quattro micro API MS using an Acquity UPLC BEH Shield RP18 column (1.7 μ m, 2.1 x 100 mm). All GC/MS experiments were conducted on a Agilent 7890A (HRGC)/5975C (LRMS) using a 15m DB-5HT column (0.25 mm id, 0.1 μ m film thickness) or a Shimadzu GCMS-QP2010 using a 30m DB-5 column (0.25 mm id, 0.25 μ m film thickness). All injections were done in splitless mode and a full scan range of 50-1000 amu was collected in positive ion electron impact mode (EI+). NMR experiments were run on a 400 MHz Bruker instrument using CDCl₂ (CDN Isotopes) or CDCl₃ (CDN Isotopes) as the solvent. Prep-TLC separations were conducted using custom plates prepared in-house.

Results and discussion

RDP

Commercially available RDP has been reported to contain 60 to 75 wt% of the P₂ species with triphenyl phosphate and higher oligomers making up the remaining 25 - 40%. It has also been reported that the levels of triphenyl phosphate in RDP are carefully controlled (usually < 5%) due to its volatile nature.⁵ The variability of these percentages, and overall lack of data on the commercial material, necessitated a more thorough characterization. LC-UV separation revealed that the technical mixture (in methanol) contained 6 main components: tentatively identified as 3.2% (suspected hydrolysis products), 4.2% (triphenyl phosphate, TPP or RDP-1), 63.2% (monomer or RDP-2), 20.8% (dimer or RDP-3), 5.3% (trimer or RDP-4), and 1.1% (tetramer). In order to determine the extent of hydrolysis of RDP in methanol, a methanolic solution of RDP was prepared and run immediately and then re-run after 5 days. Decomposition was observed with the percentages of the hydrolysis products increasing by approximately 5% (the monomer dropped by 4% and the dimer dropped by 2%). Similarly, a solution of TPP was prepared in methanol and run immediately on the LC-UV and then again after 5 days. Decomposition of TPP was also observed with approximately 9.5% of a faster running compound, presumably diphenylphosphate (DPP), appearing in the chromatogram.

A sample of technical RDP was then separated by prep-TLC into 4 fractions. A description of each fraction as well as its percentage by weight, NMR characterization, and identification are provided in Table 1. It should be noted that the volatile nature of TPP resulted in a lower percentage (by weight) than that determined by NMR indicating that some TPP may have been lost during evaporation of the solvent. NMR analysis of the RDP prep-TLC fractions allowed for definitive identification of each component.

Molar ratios obtained from the ³¹P NMR of the technical RDP mixture suggested the main components were present in the following percentages: TPP (RDP-1) 8%, monomer (RDP-2) 75%, Dimer (RDP-3) and Trimer (RDP-4) 17%. This data confirms that some TPP may have been lost during prep-TLC.

Table 1: A summary of the fractions isolated from technical RDP using prep-TLC (wt%) as well as subsequent characterization and identification.

Sample	Fraction	wt%	¹ H NMR	³¹ P NMR	Identified as
RDP	RDP-1	2-3%	yes	yes	TPP
	RDP-2	78%	yes	yes	Monomer
	RDP-3	14%	yes	yes	Dimer
	RDP-4	2-3%	yes	no	Trimer

BDP

It has been reported that BDP is more thermally and hydrolytically stable than RDP¹ therefore it was expected that the levels of observed BDP hydrolysis products would be lower during LC-UV analysis. This was indeed the case; LC-UV analysis of the technical BDP mixture indicated that it was comprised of mainly 2 components, 82.5% (monomer or BDP-1) and 15.5% (dimer or BDP-2), along with small amounts of several low-level, fast-eluting compounds including TPP. To confirm BDP's apparent increased hydrolytic stability, a solution of BDP was prepared in acetonitrile/water and run immediately and then again after 2 days and minimal decomposition was observed.

The two main components of a technical sample of BDP were separated using prep-TLC. The isolated bands (83% by weight BDP-1 and 15% by weight BDP-2) were then individually analyzed by ¹H and ³¹P NMR to identify characteristic signals of the individual components. A subsequent examination of the NMR spectra of the technical BDP material allowed for the determination of percentages of the main components. Figure 1 demonstrates the complexity of the aryl proton region in the ¹H NMR spectrum of technical BDP. Without isolation and characterization of the individual components, the signals would be difficult, if not impossible, to definitively assign. On a molar basis, the percentages were determined to be: TPP ~ 7%, monomer (BDP-1) ~

82%, and dimer (BDP-2) ~ 11%. When these numbers are converted to percentages by weight, the proportions become: TPP ~ 3%, monomer ~ 80.5%, and dimer ~ 16.5%.

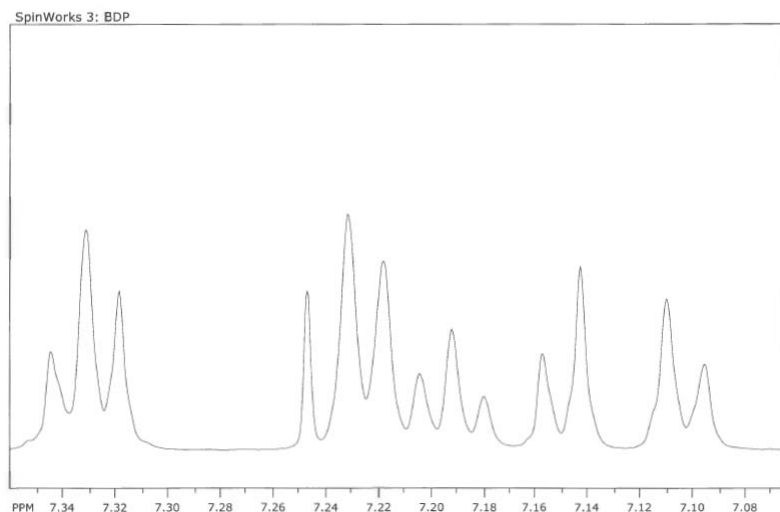


Figure 1: ^1H NMR of technical BDP; magnification of the aryl proton region.

DOPO

The LC/UV and/or LC/MS analysis of DOPO in solution is quite challenging since it can exist as multiple species (Figure 2). It has been reported that commercial DOPO (Figure 2: compound **B**) usually contains appreciable amounts (for example, 31%) of the hydrated “open-chain” phenolic phosphinic acid (Figure 2: compound **D**).⁶ This latter compound should exist largely as the anionic species in polar solvents due to the low pKa associated with benzene phosphinic acids (calculated pKa 1.65⁷), however, species **D** also contains a phenolic moiety which is susceptible to ionization. Further complicating this situation is the fact that pentavalent phosphorus compounds containing a P-H bond exhibit tautomerism, although the P(V) extreme form (Figure 2: compound **B**) usually heavily outweighs the P(III) tautomer (Figure 2: compound **A**).⁸

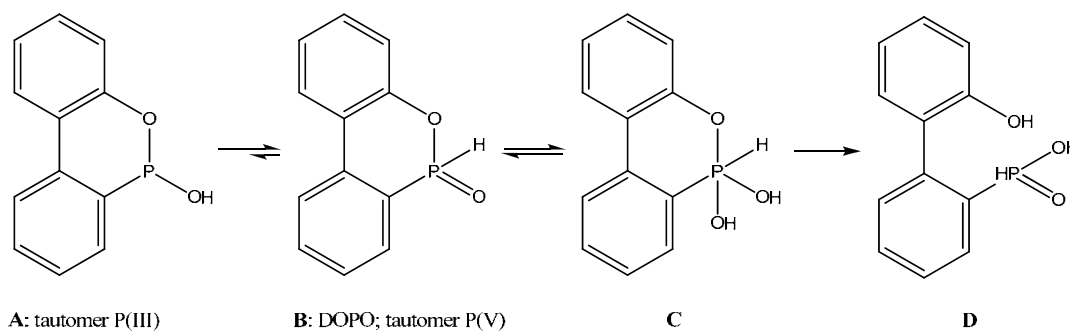


Figure 2: Possible DOPO species present in solution.

As expected, liquid chromatography of DOPO resulted in the detection of both the open and closed species, both with very poor peak shape. In order to achieve better chromatography and retain DOPO on the column for a longer period of time, a more suitable stationary phase and improved mobile phase conditions must be determined. It appears that DOPO must be forced into, and maintained in, the ring-opened form in order to avoid the generation of mixed open form species during LC analysis. Fortunately, DOPO was much more amenable to GC/MS (Figure 3). The thermally sensitive open form of DOPO appears to close when exposed to various injector port temperatures (both 250°C and 120°C were tested). This technique would be useful for determining “total DOPO” in a sample.

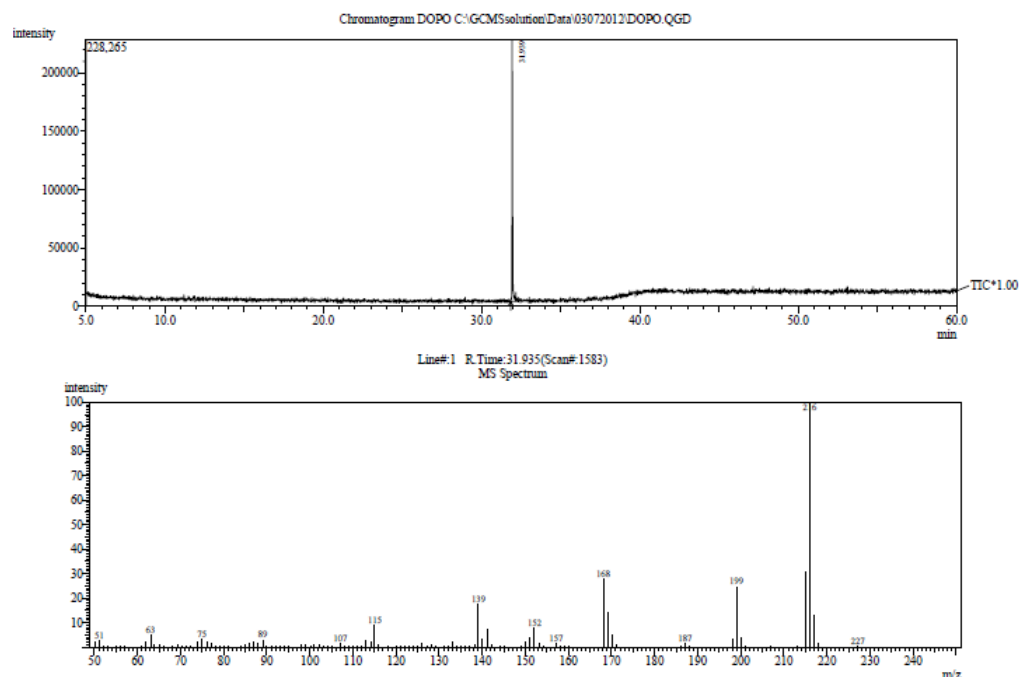


Figure 3: GC/MS chromatogram and spectrum of DOPO using a 30m DB-5 column (splitless injection at 120°C).

Various NMR experiments were also carried out to examine the behavior of DOPO in solution. A sample of technical DOPO was dissolved in CD_3OD and the resulting ^1H NMR spectrum revealed the presence of mainly two species. Integration suggested a ratio of approximately 65% of the closed form (Figure 2, B) and 35% of the open form (Figure 2, D). Also, to determine if DOPO readily opens on exposure to water, a CD_2Cl_2 solution (known to contain only the closed form species) was shaken with a few drops of D_2O and left at room temperature overnight. The ^1H NMR spectrum generated after approximately 12 hours showed a single substantial change from the initial spectrum, which was a loss of the doublet arising from the P-H proton. This outcome stems from replacement of this proton by a deuterium atom, via the tautomeric equilibrium previously discussed (Figure 2).

Acknowledgements

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References

1. Levchik SV, Weil ED. (2006); *Journal of Fire Sciences* 24: 345-364
2. Rakatomalala M, Wagner S, Döring M. (2010); *Materials* 3: 4300-4327
3. Waaijers SL, Kong D, Hendriks HS, de Wit CA, Cousins IT, Westerink RHS, Leonards PEG, Kraak MHS, Admiraal W, de Voogt P, Parsons JR. (2013); *Rev Environ Contam Toxicol* 222:1-71
4. Changzhou Chang-Yu Chemical Co., Ltd. (2013). Retrieved May 24, 2013 from <http://www.changyuchem.com/template/product4-30.htm>
5. Bright DA, Dashevsky S, Moy PY, Williams B. (1997); *Journal of Vinyl & Additive Technology* 3(2): 170-174
6. Liu Y-L, Wei W-L, Chen W-Y. (2003); *Polymer International* 52(8): 1275-1279
7. Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2013 ACD/Labs) and reported by SciFinder (<https://scifinder.cas.org/>) for p-phenyl phosphinic acid (CAS 1779-48-2).
8. Li J-N, Liu L, Fu y, Guo Q-X. (2006); *Tetrahedron* 62(18): 4453-4462