

PHOSPHORAMIDATE FLAME RETARDANTS: MECHANISM AND APPLICATION

Sabyasachi Gaan, Viktoriya Salimova, Manfred Heuberger, Patrick Rupper, Laurie Mauclaire Schoenholzer
 EMPA, Material Science and Technology, St. Gallen, Switzerland
 sabyasachi.gaan@empa.ch

ABSTRACT

Phosphoramidates are a class of organophosphorus compounds which have great potential to be used as flame retardants because of easy synthesis and efficient flame retardant action. In this research several types of phosphoramidate compounds (primary, secondary and tertiary flame retardants) were synthesized and evaluated for structure property relationships. Phosphoramidates based on methyl ester derivatives have been shown to exhibit better flame retardant action than the ethyl ester derivatives. The alkyl substitution on nitrogen atom linked to phosphorus atom has influence on the flame retardant action of phosphoramidate compounds. Further application of these phosphoramidates as flame retardants have been explored on cotton cellulose, viscose, polyacrylonitrile and cellulose acetate.

INTRODUCTION

1. Introduction

Organophosphorus compounds like phosphoramidates have a great potential in the flame retardant (FR) application for various polymeric systems. They can be easily manufactured from cheap raw materials with high yields, less volatile as compared to analogous phosphates, have good thermal stability and exhibit enhanced char formation during the burning process. The study and development of newer phosphoramidate compounds become even more important due to possible phosphorus-nitrogen (P-N) synergism phenomena. Phosphoramidates have found application as flame retardants (FRs) in various polymeric system such as polycarbonate (PC), acrylonitrile-butadiene-styrene copolymer (ABS), polyurethanes, cellulose etc[1-5].

Prior studies have shown that the action of phosphorus flame retardants may be enhanced in the presence of nitrogen. The nitrogen source could be an external additive like guanidine and urea derivatives[6] or from direct linkage of nitrogen to the phosphorus atom as in the case of the phosphoramidates[7]. Phosphoramidates have been shown to have a better flame retardant effect on cellulose as compared to phosphates in a previous study[3]. The enhanced action of phosphoramidates has been attributed to the P-N synergism phenomena. In another study the phosphoramidate structure was found to be less effective than the phosphonate structure[8]. Some studies on phosphoramidates have focused on the effect of the phosphoramidate structure on the flame retardancy of cellulose. It was shown that secondary phosphoramidates have better FR action than tertiary phosphoramidates[9]. Also the increase in the number of nitrogen atoms linked to the phosphoryl group improved the flame retardant action of the phosphoramidates

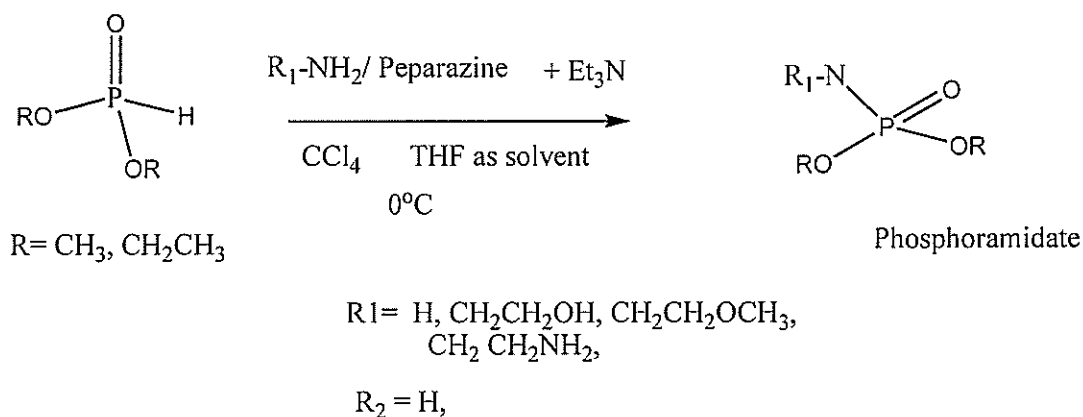
with the exception of hexamethyl phosphoric triamide [10]. More recently studies carried out on ethyl ester phosphoramidates have shown the alkyl group attached to the nitrogen atom has effect on the flame retardant properties of the FR. Hydroxyl terminating phosphoramidate has been reported to have better flame retardant properties than the methoxy and alkyl terminating phosphoramidates.

Experimental Materials.

RESULTS AND DISCUSSION

Synthesis of phosphoramidate Compounds:

The phosphoramidate compounds were synthesized using Atherton-Todd Reaction. Scheme 1 shows the general reaction conditions for synthesis of various phosphoramidates.



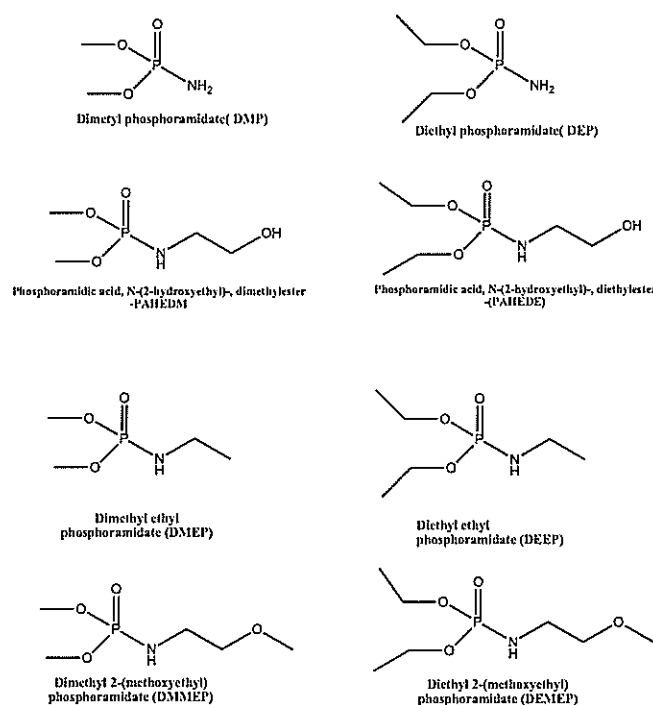
Scheme 1: Reaction conditions for synthesis of Phosphoramidates.

Scheme 2 shows the different kinds of methyl and ethyl ester phosphoramidate derivatives which were synthesized. DEP and DMP are phosphoramidates with primary amine groups. PAHEDM and PAHEDE are phosphoramidate with secondary amine group containing hydroxyl terminating alkyl groups. DEEP, DMEP and DEMEP, DMMEP are phosphoramidates containing secondary amino groups having alkyl and methoxy terminating groups respectively.

Methyl Ester phosphoramidate vs. Ethyl Ester Phosphoramidates

LOI of treated cellulose

Table 1 shows the LOI values of treated cotton cellulose with various levels of phosphorus (%P-1, 2, 4). It can be seen from the table 1 that the LOI values of methyl ester derivatives are more than the analogous ethyl ester derivatives at similar levels of phosphorus content. The LOI value of untreated cotton is 18 with no char residue. The measured char content after the LOI tests followed a similar trend. The char content after LOI tests were higher for methyl ester derivatives. This could indicate that the methyl ester derivatives have better condensed phase action as compared to ethyl ester phosphoramidates. Also phosphoramidates with primary amino (DMP, DEP) and hydroxyl terminating (PAHEDM, PAHEDE) functional groups had higher LOI and residual char as compared to phosphoramidates with alkyl (DEEP, DMEP) and methoxy terminating alkyl groups. Thus it's clear that the performance of the phosphoramidates is structure related. The alkyl chain connected to the nitrogen atom has influence on the flame retardant behavior of the phosphoramidate.



Scheme 2: List of phosphoramidates synthesized

FR	%P	LOI %	Char %
DMP	1	26.8	17.2
	2	28.8	21.8
	4	30.4	23.4
DEP	1	23.3	8.5
	2	25.5	12.2
	4	27.8	17.8
PAHEDM	1	25.5	15.4
	2	27.5	19.4
	4	31.2	24.9
PAHEDE	1	24.2	10.8
	2	26.6	16.2
	4	28.7	23.8
DMEP	1	25.5	18.4
	2	27	19.6
	4	28.9	20.5
DEEP	1	23.5	13.9
	2	25.7	15.8
	4	27.3	18.5
DMMEP	1	25.5	18.4
	2	27	19.6
	4	28.9	20.5
DEMPEP	1	22.2	7.7
	2	24.3	11.5
	4	26.3	22.8

Table1: Burning behavior of Phosphoramidate treated cotton cellulose: LOI and Char content

PCFC data of treated cellulose

Effect of alkyl substitution on flame retardant behavior of ethyl ester derivatives

It was observed in table 1 that the flame retardant values of ethyl ester derivatives differ and is dependent on the substituent on nitrogen atom. The primary phosphoramidate DEP and secondary phosphoramidate PAHEDE has better flame retardant properties than secondary phosphoramidates DEMEP and DEEP. We investigated this phenomena further using TGA-FTIR and TGA-MS.

TGA-FTIR data

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