The Thermal Degradation Pathway Studies of a Phosphazene Derivative on Cotton Fabric

Krystal R. Fontenot,¹ Monique M. Nguyen,¹ M. Sameer Al-Abdul-Wahid,² Michael W. Easson,^{1*} SeChin Chang,¹ Gary A. Lorigan,² Brian D. Condon¹

¹Cotton Chemistry and Utilization Research, United States Department of Agriculture, 1100 Robert E. Lee Blvd. New Orleans, LA 70124

²Department of Chemistry and Biochemistry, Miami University, 701 E. High St. Oxford, Ohio 45056

*Correspondence email: michael.easson@ars.usda.gov

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ABSTRACT

Phosphazene derivatives have been recognized as promising flame retardants for numerous synthetic polymeric systems. However, limited studies are available for phosphazene derivatives on natural polymeric systems such as cotton fabric. The flammability and thermal stability of fabric treated with a phosphazene derivative 1,1,3,3-dihydroxybiphenyl-5,5-diaminogethanephosphazene (dBEP) indicated that only 9 wt% of dBEP was required to achieve promising flame retardant properties on cotton fabric. To understand the mode of action of dBEP, the thermal degradation pathways of the control and cotton fabric treated with dBEP were investigated. Thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA-FTIR) was used to follow the evolved gases produced by the control and treated fabrics during thermal degradation. Two techniques attenuated total reflectance infrared spectroscopy (ATR-IR) and solid-state nuclear magnetic resonance (NMR) were employed to examine the degraded residues of the unburned fabrics, burned fabrics, and dBEP. The results show that dBEP undergoes decomposition to produce phosphoric acid and polymerization to form phospham-like derivative that are known to retard fire.

1. INTRODUCTION

Flame retardants (FRs) act as a barrier to inhibit, delay, or suppress the burning process of materials in order to prevent the spread of fire.[1] The applications of FRs have varied over the

years from wood, furniture, upholstery, children's clothing, and aircrafts.[2,3] There is a growing interest in understanding the thermal behavior, flammability properties, and mechanistic behavior of FRs. Various techniques such as thermogravimetric analysis (TGA), limiting oxygen index (LOI), 45 degree flammability test, and microscale combustion calorimetry (MCC) have been used to determine the thermal and flammability behavior of FRs. While these techniques are informative tools used to investigate properties of FRs, very little is known about the degradation behavior of FRs.[4] As interest in the thermal degradation of FR compounds increases, techniques such as gel permeation chromatography (GPC), vapor phase chromatography (VPC), mass spectrometry (MS), and flow-tube depolymerization (FTD) have been used to study FR mechanisms.[5] Currently, a combination of techniques including pyrolysis gas chromatography/mass spectrometry (Py-GC/MS), thermogravimetric analysis coupled to Fourier transform infrared spectroscopy (TGA-FTIR), and solid-state cross polarization/magic angle spinning nuclear magnetic resonance spectroscopy (CP/MAS-NMR) have been used to study FRs, cellulose, and cellulose related products such as microcrystalline cellulose, wood, and fabric.[6-9] Studying the thermal decomposition of a FR provides identification of the degradation pathway and the products produced in the gas and solid phases that retard fire. In general, mechanism studies of FRs are limited, but an even smaller number of studies focus on phosphazene-based FRs.

Phosphazene-based FRs consist of phosphorus and nitrogen elements that are known to exhibit better FR properties that include high char yield and LOI values, lower onset temperatures, and the production of flame inhibiting products.[10-12] There are different types of phosphazene derivatives such as poly and cyclo-phosphazenes which have been investigated for its flammability, thermal stability, and degradation pathway.[13-15] Although polyphosphazenes were investigated for their flammability and thermal behavior on cotton fabric,[16-18] their degradation pathways have been determined independently of cotton fabric. These derivatives are known to have different decomposition mechanisms in polymeric systems such as the exocyclic pathway, endocyclic pathway, ring equilibration, random chain scission, polymerization, depolymerization, and ring expansion that are determined by the substituents on the phosphazene ring.[19-26] Smaller side groups are known to favor the polymerization process while larger side groups favor the depolymerization process.[21,27] Although, the mechanistic

behaviors of polyphosphazene derivatives have been studied independently, there are limited studies available regarding their use as an inherent FR on natural polymeric systems such as cotton fabric. [28-31]

In our earlier paper a phosphazene derivative 1,1,3,3-dihydroxybiphenyl-5,5-diaminoethanephosphazene (dBEP) was studied for its flammability and thermal stability properties and was shown to be an effective FR for cotton fabric.[32] At a low add-on of 9 wt% the treated fabric did not ignite for the 45 degree angle test, had a high LOI value of 27%, a high char yield of 37%, and a low onset temperature of 312°C.[32] In our present paper the mode of action of dBEP on cotton fabric was investigated using a combination of techniques such as TGA-FTIR to examine the gas phase and attenuated total reflectance infrared spectroscopy (ATR-IR) and solid-state total sideband suppression cross polarization nuclear magnetic resonance spectroscopy (TOSS-CP-NMR) to study the solid phase. The interpretation of these analytical results provided an overall view of the thermal degradation pathway of dBEP and is reported herein.

2. EXPERIMENTAL

Dichloromethane (DCM), methanol (MeOH), isopropyl alcohol (IPA), ethanol (EtOH), ethyl acetate, acetone, hexanes, and anhydrous potassium carbonate (K_2CO_3) were purchased from Fisher Scientific. All chemicals were used as received without further purification. Cotton fabric (100%) was purchased as twill fabric style 423 with the weight of 258 g/m² from Test Fabrics, Inc. The fabric was desized, bleached, and was free of all resins and finishes.

2.1 Synthesis and Fabric Treatment. Compound dBEP (Figure 1a) was synthesized and characterized according to the reported procedure.[32] ¹H NMR (400 MHz, acetone-*d*₆) δ 7.66 (*m*, 4H), 7.49 (*m*, 4H), 7.36 (*t*, 8H, *J* = 8.1 Hz), 3.84 (*d*, 2H, *J* = 9.6 Hz), 3.26 (*d*, 4H, *J* = 12.4 Hz). ¹³C NMR (101 MHz, CH₂Cl₂-*d*₆) δ : 149.0 (*s*), 129.9 – 129.6 (*s*), 129.3 (*s*), 126.0 (*s*), 122.4 (*s*), 115.6 (*s*), 42.7 (*d*). ³¹P NMR (162 MHz, CD₂Cl₂-*d*₆) δ : 34.79 – 33.94 (*t*, 1P, P(NH₂CH₂)₂), 28.80 – 28.27 (*d*, 2P, P(O₂C₁₂H₈)₂).

Twill fabric (2.5 x 6) was immersed in a shallow pan containing a solution of dBEP in DCM/acetone (1:1) to obtain a percent add-on of 22 wt%. After soaking for 5 minutes, the fabric was padded at 10 psi (Birch Bros. Southern Inc.), dried at 100°C for 5 minutes (W. Mathis AG Dryer LTF.), and cured at 160°C for 1.5 minutes (Mathis Lab dryer LTE.). After removal from the oven, the fabric was allowed to cool to room temperature and the add-on value was calculated using equation (1).

$$\text{Add - on (\%)} = [(w_{\text{after treatment}} - w_{\text{before treatment}}) / (w_{\text{before treatment}})] \times 100 \quad (1)$$

2.1 Attenuated total reflectance infrared (ATR-IR). A Platinum Alpha ATR-IR Bruker spectrometer, A220/D01 was used to determine the functional groups of the control and treated fabrics before thermal degradation and at 250, 275, 300, 320, and 375°C. One hundred forty scans at a resolution of 4 cm⁻¹ were recorded for each sample between the 4000 – 500 cm⁻¹ region, and the spectra were analyzed using OPUS 6.5 software.

2.2 Thermogravimetric analysis – Fourier transform infrared (TGA-FTIR). Thermogravimetric analysis (TGA) was performed using a TA Instruments Q500 under nitrogen. Sample masses of 4.0 – 8.0 mg were heated from 25 – 600°C at a rate of 10°C/min. The FTIR experiment was conducted on a Bruker Tensor 27 between 100 and 600°C under nitrogen with a 4 cm⁻¹ resolution in the 4000 – 600 cm⁻¹ region. The signals were measured using a liquid nitrogen cooled MCT detector with a ZnSe window. Both lines transferring the evolved gasses from TGA to FTIR and to the IR sample cell were maintained at 200°C. The FTIR data were collected at five degree increments during the experiment and analyzed using Opus software (version 6.5), which measures the intensity of the absorption band as a function of temperature. The FTIR spectra were supported by Origin Lab 8.6 software which depicted the original three dimensions for analysis purpose.

2.3 Solid-state nuclear magnetic resonance (solid-state NMR) studies of the control and treated fabrics and dBEP. Unburned and 320°C samples of the fabrics and dBEP were evaluated using solid-state NMR. The samples were placed into a coorstek crucible with a perforated bottom that was lined and sealed with aluminum foil. The crucible was then placed

into a Thermo Scientific Thermolyne oven F6000 furnace and heated at a flow rate of 15°C/min under nitrogen flow of 40 psi. The control fabric, treated fabric, and dBEP were heated to 320°C. The unburned and 320°C samples were ground using a Wiley Mill and dBEP was separately ground using a mortar and pestle. Solid-state NMR experiments were obtained using a Bruker Avance 500 MHz (11.7 T) wide-bore spectrometer equipped with a doubly-tuned cross polarization magic angle spinning (CP/MAS) probe. Each sample was packed into a 4mm rotor. ¹³C-TOSS-CP-NMR spectra were collected using total sideband suppression cross polarization (TOSS-CP) with 8192 transients at a spinning speed of 7 kHz.

3. RESULTS AND DISCUSSION

3.1 Synthesis and fabric treatment. All starting materials were commercially available for the synthesis of the phosphazene derivative 1,1,3,3-dihydroxybiphenyl-5,5-diaminoethanephosphazene (dBEP). The synthesis was achieved in a two-step reaction by reacting phosphazene with 2,2'-dihydroxybiphenyl in the presence of acetone and K₂CO₃ at 0°C and allowing the reaction to warm to room temperature under inert conditions. The reaction was then filtered, concentrated, and purified by trituration with hexanes.[32,35] The intermediate was reacted with 1,2-diaminoethane in DCM at 0°C and allowed to warm to room temperature under inert conditions.[32,35] The organic layer was extracted with water, concentrated, and the final product, dBEP, was achieved with a yield of 76%.[32] Furthermore, the solubility test of dBEP was performed using MeOH, IPA, EtOH, acetone, ethyl acetate, and DCM. The best solvents to dissolve dBEP were a mixture of DCM and acetone (1:1). The structure of dBEP, as shown in Figure 1A, is comprised of a phosphazene ring having two spirocyclic structures of 2,2'-dihydroxybiphenyl at the first and third position and one spirocyclic structure of 1,2-diaminoethane at the fifth position.

The phosphazene derivative, dBEP, was applied to 100% cellulose cotton twill fabric as a coating using a pad-dry cure method and will be referred to as the *treated fabric*. After the treatment, the fabric was slightly stiff and retained a white color. The high add-on of 22 wt% was used to ensure that volatile gases were detected during combustion.[8,9] The untreated fabric

used in this study is 100% cellulose cotton twill fabric which is comprised of a polymeric chain of glucose units (Figure 1B) and this will be identified as the *control fabric*.

3.2 Functional groups observed for fabrics and dBEP. Figure 2 shows the functional groups of the unburned fabrics and dBEP that were identified using ATR-IR. The ATR-IR of the control fabric has been well studied and evaluated for its functional groups.[36-38] Characteristic bands of the control includes the broad O—H band with a stretching frequency of 3296 cm^{-1} , the C—H, C—H₂ bands at 2893 cm^{-1} , 1426 cm^{-1} , $1364 - 1313\text{ cm}^{-1}$, and 893 cm^{-1} , the C—O band at 1021 cm^{-1} , and C—C bands at 665 cm^{-1} . [39,40] These functional groups support the six membered rings with hydroxyl groups (Figure 1B). The peak at 1640 cm^{-1} indicates absorbed water molecules. Other bands corresponding to the ATR spectra along with literature references of cotton fabric are given in Table S1 of the supporting information.[36-40]

The functional groups of dBEP were represented by intense bands at 3394 cm^{-1} , 3063 cm^{-1} , and 2875 cm^{-1} which represent N—H, Ph—H, and C—H, respectively.[34,41,42] The aromatic ring has symmetrical stretching frequencies at $1499 - 1437\text{ cm}^{-1}$ and 1089 cm^{-1} . [34] The presence of the aromatic ester bond (P—O—Ar) between 2,2'-dihydroxybiphenyl and phosphazene resulted in two frequencies of 1162 and 943 cm^{-1} . [27,42,43] The aromatic ester bond is further supported by the O—P—O band at 789 cm^{-1} . [42,43] The band representing the phosphazene moiety has P=N—P bonds where P=N has a vibration frequency of $1264 - 1225\text{ cm}^{-1}$ and a stretching vibration (N—P) at 849 cm^{-1} . [34,41,42,44-47]. The P—N—C, C—H₂, and N—P—N bands of the phosphazene ring bonded to ethylenediamine have stretching vibrations of the N—C bond present at 1187 cm^{-1} . [34,44,45,47-51] The C—H₂ bonds have a symmetrical stretching frequency of 2875 cm^{-1} with out of the plane deformations at 749 cm^{-1} and 667 cm^{-1} . [34,45] Similar structures were used to ascertain the IR frequency of N—P—N bonds formed between phosphazene and diaminoethane, at 607 cm^{-1} frequency. [52,53] The ATR-IR spectra confirmed the functional groups that correspond with dBEP and the assignments of dBEP are in agreement with the literature (Table S1 in supporting information.) [34,41,42,44,45]

The ATR-IR spectra of the treated fabric contained overlapping characteristic bands between dBEP and the cotton fabric. As a result, only the following bands are observed: the broad O—H

band with a stretching frequency of $3400 - 3100\text{ cm}^{-1}$, the C—H, C—H₂ bands at $2893 - 3000\text{ cm}^{-1}$ and $1364 - 1313\text{ cm}^{-1}$, and the C—O band at 1021 cm^{-1} . [39,40] The bands that were not observed due to overlapping are the C—H, C—H₂ bands at 893 cm^{-1} and C—C bands at 665 cm^{-1} . Although the control fabric has bands around 665 cm^{-1} and 607 cm^{-1} , it does not correspond to the 665 cm^{-1} and 607 cm^{-1} band observed for the treated fabric, as these bands are seen in dBEP. The ATR-IR spectra confirmed the functional groups that correspond with cotton fabric, treated fabric, and dBEP. It can be concluded that dBEP remained structurally intact after the cotton fabric was treated.

3.3 Summary of flammability and thermal stability. Previously we reported the 45 degree flammability test, limiting oxygen index test (LOI), and thermogravimetric analysis (TGA) test which determined the flammability and thermal stability of dBEP at various additive loadings of 6, 9, 12, 16, and 22 wt%. [32] Figure 3 shows the 45 degree flammability test and the LOI test results of the control and treated fabrics. 45 degree testing evaluates the ability of fabric to resist burning at an angle when exposed to open flames. [33] Treated fabrics with a minimum add-on of 9 wt% are classified as Class I fabrics and resulted in a reduced burning rate compared to the control. [32] The LOI experiment, determines the minimum amount of oxygen required for fabric to burn in the presence of flowing oxygen and nitrogen gas. [34] Fabrics with a 9 wt% and higher are self extinguishing. [32]

The thermal stability of the treated fabrics was evaluated using TGA (Figure 4), which measures the change in mass with respect to temperature. [32] The results from TGA indicated that an additive loading of 9 wt% was effective to achieve a high char yield of 37%. The control fabric exhibited a broad degradation range between $275 - 375^{\circ}\text{C}$ with a 15% char yield, whereas the treated fabric (9 – 22 wt%) exhibited a one-stage degradation with a sharp descent in mass between $310 - 318^{\circ}\text{C}$ and a 39% char yield. The char yield (15%) of the control fabric was lower than the char yield (39%) obtained for the fabric treated with dBEP. Phosphazene-derived systems such as polyphosphazenes with and without aliphatic chains $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$ and $[\text{NP}(\text{OC}_6\text{H}_4\text{CH}_3\text{-p})_2]_n$ have exhibited the same sharp behavior observed for the treated fabric. [19,54] Additionally other structures such as $[\text{NP}(\text{OC}_6\text{H}_4\text{NH}_2)_3(\text{tertbutyl})_3]_3$ and $[\text{NP}(\text{OC}_6\text{H}_5)_6]_3$ have also shown similar behavior. [19,31] The onset temperature of the control

fabric (331°C) is higher than the onset temperature of the treated fabrics (310 – 318°C). Independent of the cotton fabric, dBEP has a higher char yield of 54% and displays three different onset-temperatures: 343, 437, and 523°C. The onset-temperature of the control fabric (331°C) decreases to 310 – 318°C with the addition of dBEP (treated fabric). Overall, the application of dBEP on the cotton fabric improves the char yield and alters the onset temperature of the fabric. These findings support dBEP as a promising flame retardant for cotton textiles and as a result, its degradation pathway on cotton fabric was investigated. For the purpose of this paper only the treated fabric with a 22 wt% add-on will be used in the following studies.

3.4 Functional groups observed for gas products. The TGA coupled with FTIR was used to determine the functional groups of the real-time gaseous products generated during thermal degradation.[39] The three dimensional FTIR spectra of the control and treated fabrics are shown in Figures 5 and 6. All fabrics were evaluated depending on their degradation temperature range.

As the temperature of the control fabric ramped from 100°C to 600°C, evolved gases were observed and identified by functionality. As this occurred, the hydrogen bonds in the cotton fabric are ruptured, water is generated, the super molecular structure of cellulose is modified, and the amorphous region is damaged.[39] The generation of free radicals may appear in this stage.[39,55] In the 375 – 475°C degradation temperature range of the control, water (4000 – 3750 cm⁻¹), O—H (3450 – 3000 cm⁻¹) and C—H from alkanes and aldehydes 3000 – 2800 cm⁻¹ indicates that highly flammable gases such as levoglucosan, furan, furfural and methane are produced.[55] This results in oxygenation, dehydrogenation, and decarbonization which accelerates the combustion of the control fabric.[39] The bands at 2400 – 2300 cm⁻¹ and 2350 – 2000 cm⁻¹ represent CO₂ and CO gases, respectively.[39] The intense C=O band ranging from 1850 – 1600 cm⁻¹ indicates that ketones, aldehydes, and carboxylic acid based gases are released.[39] Frequencies of 1500 – 900 cm⁻¹ refer to the in-plane flexure vibration of C—H and the skeletal vibration of C—O and C—C, respectively.[39,40] Products like tar, char, and light gases are produced during the main decomposition of the control.[39] Finally, the releases of water, O—H, and CO₂ gases are still observed. Overall, the observed functional groups of the released flammable gases confirm the combustion and the progressive degradation of the cotton fabric.

255
 256 The only bands observed for the treated fabric occurs during the main pyrolysis around 315°C.
 257 Figures 6A and B show that no major bands were observed before or after 315°C. From 100 –
 258 300°C, the FTIR spectrum of the treated fabric, as shown in Figure 6C, exhibited a gradual
 259 release of water (4000 – 3750 cm⁻¹ and 1800 – 1500 cm⁻¹), O—H (3450 – 3000 cm⁻¹), and CO₂
 260 (358 – 2310 cm⁻¹) from the cotton fabric.[39,40] As this occurs, the treated fabric is undergoing
 261 dehydration which continues through decomposition. During the main degradation of 315°C, a
 262 rapid and sharp release of N—H and N—H₂ groups from amines 3750 – 3450 cm⁻¹, O—H
 263 groups from hydroxyl 3450 – 3000 cm⁻¹, and C—H bands from aromatic compounds and cotton
 264 fabric are present at 3100 – 2800 cm⁻¹. [34,41,42] The generation of primary and secondary
 265 amines could be due to the cleavage of a diaminoethane bond at the fifth position of dBEP.[19]
 266 The presence of aromatic bands 3000 – 2800 and 1600 – 1400 cm⁻¹ indicates that the 2,2'-
 267 dihydroxybiphenyl at the first and third position of dBEP are cleaving during combustion.
 268
 269 The degradation of 1,2-diaminoethane produces gases such as methanamine, ethanamine,
 270 diethyl-1,2-ethaneamine, and ammonia. The amino gases released during combustion are
 271 represented by the N—C, N—H, and C—H bands at 1195 cm⁻¹, 828 cm⁻¹, 753 cm⁻¹ and 669 cm⁻¹,
 272 respectively.[8,34,45,47-51,56] Deformations of the secondary amines and P—NH₂ range from
 273 1650 – 1550 cm⁻¹ and 992 – 907 cm⁻¹, respectively.[8,51] The P=N bonds observed at 1249 cm⁻¹
 274 could be indicative of the phosphazene ring cleavage during combustion.[8] Phosphorous and
 275 nitrogen FRs are known to interact in the gas and solid phase during the combustion
 276 process.[3,12,57,58] These gases can further react to produce solids such as carbamates,
 277 phosphoramidite, and phosphoric acid that are known for their FR properties.[8] The presence of
 278 these structures would be located in the char layer, thus acting as a protective barrier that shields
 279 or delays the cotton fabric from burning. Aromatic structures such as hydroxybenzene and
 280 phenylamine may be present due to the characteristic aromatic bands in the ring vibration region
 281 between 1600 – 1400 cm⁻¹, which include the 1507 cm⁻¹ and the 1103 cm⁻¹ bands.[34]
 282
 283 More CO₂ and CO gases are released from the fabric and dBEP at 2358 – 2310 cm⁻¹ and 2185 –
 284 2115 cm⁻¹, respectively.[39,40] Molecules containing a P=O moiety are potentially indicated by
 285 the band at 1769 – 1700 cm⁻¹. [8] Overall, the TGA and FTIR spectra show similar behaviors for

the control and treated fabrics. For instance, the degradation temperature for the control fabric in Figures 4 and 5 expand over one-hundred degrees ranging from 275°C – 375°C and 375°C – 475°C, respectively. In comparison, the degradation temperature for the treated fabric in Figures 4 and 6 covers a narrow range 310 – 318°C and approximately 315°C, respectively. The temperature ranges observed by TGA are complemented by the FTIR spectra of the control and treated fabrics. Table S2 in the supporting information list the wavenumber and assignments of the control and treated fabric.

3.5 Functional groups detected from residues of the treated fabric at various temperatures. The spectroscopic technique, ATR-IR, was employed to examine the appearance and disappearance of the functional groups of the pyrolyzed treated fabric. The treated fabrics were pyrolyzed using TGA at 250°C, 275°C, 300°C, 320°C, and 375°C (Figure 7). Characteristic bands of the control and treated fabrics were previously discussed in Section 3.2. The functional group assignments can be found in Table S3 of the supporting information.

At 250°C, which is below the onset-temperature of 318°C, the treated fabric undergoes very little degradation and subtle peak shifts are observed. The spectra of the 250°C treated fabrics shows a combination of the control and treated bands. Characteristic fabric bands observed are: the O—H band with a stretching frequency of 3400 – 3100 cm⁻¹, the C—H and C—H₂ bands at 2893 – 3000 cm⁻¹ and 1361 – 1313 cm⁻¹, and the C—O band at 1021 cm⁻¹. [39,40] The N—H, O—H, Ph—H, and C—H are represented from 3650 – 2870 cm⁻¹. The aromatic carbons of the 2,2'-dihydroxybiphenyl are present at 1499 – 1437 cm⁻¹ and 1091 cm⁻¹, respectively. [34] The presence of O—P—O at 781 cm⁻¹ supports the bonds formed between phosphazene and 2,2'-dihydroxybiphenyl. [42,43] The P—O—Ar bands at 1169 cm⁻¹ and 924 cm⁻¹ indicate that the aromatic structure is still intact. Bands corresponding to phosphazene and 1,2-diaminoethane bonds are P=N (1265 – 1227 cm⁻¹), N—C (1187 cm⁻¹), P—N (853 cm⁻¹), C—H (751 and 666 cm⁻¹), and N—P—N (608 cm⁻¹), respectively. [8,34,45,47-51,56] At 250°C, the fabric and dBEP are thermally stable.

As the temperature increases to 275°C, minor modification to the structure of the treated fabric will occur since this temperature remains below the onset-temperature of 318°C. In the 3650 –

1800 cm^{-1} region, broader bands are observed which indicates modification of the cotton fabric and the formation of new bands, Figure 7. These bands refer to an increase in N—H, O—H, C—H, and Ph—H while the formation of new bands in the 2800 – 2050 cm^{-1} range refer to the formation of P(=O)—OH functional group, which generally indicates organophosphorus compounds.[8,59] Furthermore, the P(=O)—OH moiety is also supported by the bands at 1704 – 1695 cm^{-1} and 1008 cm^{-1} . [59] Also, the peak at 1582 cm^{-1} refers to a compound containing the P(=O)-NH₂ functionality.[47] These bands imply that compounds containing P=O groups are present in the residue layer. The degradation of the treated fabric results in the masking of characteristic fabric bands such as C—H (1361 – 1313 cm^{-1}), C—O (1021 cm^{-1}), and C—H (893 cm^{-1}). Aromatic bands present at 1496 – 1434 cm^{-1} and 1081 cm^{-1} represent aromatic compounds present in residue layer.[34] The shift of the P=N band at 1243 cm^{-1} and the absence of the P—N band at 853 cm^{-1} suggest that the phosphazene ring has opened, thereby allowing smaller compounds to form.[23,31,60] Two characteristic bands indicative of the P—O—Ar functionality at 1169 cm^{-1} and 948 cm^{-1} are observed but the former band may be masked by the shoulder band at 1188 cm^{-1} . This may signify that some of the P—O—Ar bonds were cleaved, while some of the bonds remained intact at 275°C, which is supported by the presence of the O—P—O bonds at 789 cm^{-1} . The cleaving of some P—O—Ar bonds validates the hypothesis that aromatic molecules are released in the gas phase, Figure 6. Evidence of the 1,2-diaminoethane moiety is represented by the N—C (1188 cm^{-1}) and C—H (755 cm^{-1}) bands, although the P—N (853 cm^{-1}) and C—H (669 cm^{-1}) bands are masked. This indicates the structure at the fifth position of phosphazene is still intact and is further supported by the N—P—N peak at 608 cm^{-1} .

Fabrics pyrolyzed at 300 – 375°C have similar bands that vary in intensity as the temperature increases. Bands in the 3650 – 1800 cm^{-1} range of the 300 – 375°C spectra refer to the same bands that were observed in the 275°C spectrum. The P=O groups have more intense bands with a slight shift to 1704 – 1698 cm^{-1} and 1583 cm^{-1} . The P—O—Ar bands are reduced in size while other characteristic aromatic carbon bands, with a subtle shift, remain at 1495 – 1434 cm^{-1} and 1081 cm^{-1} . This suggests that the P—O—Ar bonds are potentially cleaved between 275°C and 300°C, which further supports the production of volatile aromatic compounds. Furthermore, aromatic carbon bands present in the residue layer between 300 – 375°C may represent products

like 2-phenylphenol and biphenol. The O—P—O functionality observed in the 300 – 375°C spectra at 789 cm⁻¹ remains in the residue layer and represents an organophosphorus structure (Figure 7). The shoulder peak at 1243 cm⁻¹ that was once attributed to the P=N bond for phosphazene may now represent the functionality of a phosphorus-nitrogen structure which continues to be present from 300 – 375°C. Other bands such as N—C (1188 cm⁻¹) and N—P—N (607 cm⁻¹) were also continuously present at 300 – 375°C. The ATR-IR spectrum of the pyrolyzed treated fabric shows that compounds containing P=O, O—P—O, and N—P—N functionalities are present in the residue layer. Complementary results from TGA (Figure 4) support the degradation of the fabric from 300 – 375°C since its onset-temperature ranges from 308 – 318°C.

3.6 Solid-state NMR studies of control and treated fabrics and dBEP. The appearance and disappearance of characteristic carbons in the unburned and 320°C fabrics, and dBEP were evaluated using total sideband suppression cross polarization nuclear magnetic resonance (¹³C-TOSS-CP-NMR). The 320°C temperature was selected because it is close to the onset of degradation of the treated fabric. The ¹³C-TOSS-CP-NMR of the fabrics and dBEP are shown in Figure 8. Signals of the fabrics and dBEP are listed in Table S4 in the supporting information. Considerable differences were observed between the unburned and 320°C control and treated fabrics and dBEP.

The unburned control has hydroxyl and aliphatic functionality that correspond to signals for C₁ at 108.6 – 101.0 ppm, C₄ at 90.9 – 80.0 ppm, C₅, C₃, and C₂ at 78.1 – 69.3 ppm, and C₆ at 66.6 – 59.0 ppm that are in agreement with literature values.[61,62] The fabric at 320°C gave rise to two highly broadened signals at 169.1 – 106.5 ppm and 68.0 – 13.0 ppm indicating the formation of compounds characteristic of cellulose char in the aromatic region (C_{AR}) and alkyl region (C_{ALK}) of the spectrum, respectively.[6,63] The absence of characteristic fabric signals representing the C₁, C₄, C₃, C₂, and C₆ positions of the glucose unit of cellulose indicate that structural changes are occurring with the potential loss of C—O bonds.[6] The 320°C control fabric residue has similar signals to other cellulose related residues such as the microcrystalline cellulose and Kraft paper containing 90% cellulose and a 10% combination of pentosans and lignin.[6,63]

The unburned dBEP gives rise to three sets of strong signals, assigned as C_O (C—O, aromatic) at 148.3 ppm, C_{AR} (C—H) spanning 134.7 ppm – 117.2 ppm, and C_{ALK} (C—H) at 42.6 ppm. The chemical shifts of dBEP agree with the phosphazene derivative poly[bis(4-ethylphenoxy)phosphazene] ($[NP(OC_6H_4CH_2CH_3)]_N$).^[64] The 320°C dBEP has similar signals as unburned dBEP, although a greater number of sharper signals are observed in the 320°C dBEP spectrum. This may result from rearrangement of the dBEP into more uniform crystal structure, or may be simply due to improved homogeneity of the NMR sample.

The unburned treated spectrum has signals arising from the unburned control and dBEP. Signals at 148.7 ppm, 134.1 – 117.4 ppm, and 43.5 arise from C_O , C_{AR} , C_{ALK} of 2,2'-dihydroxybiphenyl moiety on cotton fabric; whereas, the C_1 at 109.2 – 98.7 ppm, C_4 at 91.6 – 79.6 ppm, C_5 , C_3 , and C_2 at 79.6 – 68.3 ppm, and C_6 at 67.9 – 57.7 ppm are attributed to the fabric. This data further supports the conclusion that dBEP and the fabric remain chemically unchanged after the treatment process.

Morphological differences were observed for the 320°C treated which includes the appearance and disappearance of signals, Figure 8. The C_O and C_{AR} signals for dBEP are broader than the unburned treated fabric, suggesting the transformation of the aromatic species caused by the degradation of cotton fabric and dBEP. The dBEP C_{ALK} signal has broadened into the baseline and is not observed. The presence of a very broad signal at 54.9 – 8.1 ppm is consistent with cellulose char (C_{CHAR} , 169 – 107 ppm and 68 – 13 ppm) and indicates that some of the control fabric is degrading. However, the signals of the unburned control (cellulose) are prominent and unchanged in chemical shift, indicating that dBEP protected the fabric from complete degradation, and supports the conclusion drawn from ATR-IR data (Figure 7, 275°C). Complementary findings from solid-state NMR and ATR-IR analysis support the functionalities of aromatic and amino products even though each technique determines the functionalities differently.

3.7 Possible thermal degradation pathway of dBEP. A plausible degradation pathway of the treated fabric is proposed based on the ATR-IR, TGA-FTIR, and solid-state NMR findings. It

has been reported that the substitution of halogens, alkyls, aryls, alkoxy, aryloxy, and amines on the phosphazene ring determines its degradation pathway.[19,21,25-27] For example, tris(2,2'-dioxyphenyl)cyclotriphosphazene $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)_3]_3$ and hexaphenoxycyclotriphosphazene $[\text{NP}(\text{OC}_6\text{H}_5)_6]_3$ are substituted with three 2,2'-dihydroxybiphenyl and six hydroxybenzene on the phosphazene ring, respectively.[65,66] Tris(2,2'-dioxyphenyl)cyclotriphosphazene and hexaphenoxycyclotriphosphazene are stable and do not polymerize when heated to 300°C or 350°C, respectively, for long periods of time.[65,66] These phosphazene derivatives favor decomposition mechanism due to the bulky nature of the organic side groups.[21,27] Examples of aminocyclophosphazenes include hexaaminocyclotriphosphazene $[\text{NP}(\text{NH}_2)_2]_3$ and anilino-cyclophosphazenes $[\text{NP}(\text{NHPh})_2]_3$, which are substituted with six amines and phenylamines, respectively. These aminophosphazenes pyrolyze to phosphams by a condensation-polymerization reaction and depending upon its substituents it releases ammonia or hydrogen chloride gases.[20,67-69]

Since there are structural similarities between aryloxy and amino cyclophosphazene derivatives and dBEP, they will be used to explain the degradation pathway of the treated fabric. The structure of dBEP $[\text{NP}(\text{O}_2\text{C}_{12}\text{H}_8)_2(\text{N}_2\text{C}_2\text{H}_6)]_3$ is comprised of a phosphazene ring having two spirocyclic structures of 2,2'-dihydroxybiphenyl at the first and third position and one spirocyclic structure of 1,2-diaminoethane at the fifth position. Phosphazene with similar bulky substituents, namely tris(2,2'-dioxyphenyl)cyclotriphosphazene and hexaphenoxycyclotriphosphazene, were reported to favor decomposition instead of polymerization. Thus, the 2,2'-dihydroxybiphenyl moieties in dBEP are decomposing into smaller systems and are less likely to polymerize on the treated fabric.[21,27,65,66]

Scheme 1 illustrates the degradation pathway for dBEP, which initiates with the cleavage of one C—O bond from each of the two biphenyl groups at the first and fifth positions. The dBEP structure undergoes thermal decomposition to generate a species containing P=O that will cleave the O—C bond on the aromatic ring to form a phosphoramidite (**1**). Water is then generated from the combustion process between dBEP and the fabric, which can nucleophilically attack the P=O group to break open the phosphazene ring and form a phosphoramidite-like (phosphonate) structure (**2**) and a phospham-like structure (phosphine) (**3**). The 2,2'-dihydroxybiphenyl

structure may cleave at the carbon bond in the gas phase to produce hydroxybenzene and phenylamine, which have a boiling point of 181°C and 184°C, respectively. The volatile releases of the aromatic structures are supported by TGA-FTIR. The results of ATR-IR, TGA-FTIR, and solid-state NMR confirm that dBEP is decomposing. Products (2) and (3) are reactive intermediate species that will continue in the degradation pathway. Product 2 reacts with water to produce another O—H functionality that forms a phosphoric acid-like structure and releases a primary amine that can react in the gas phase to produce ammonia (4). Compounds such as phosphoric acid and polyphosphoric acid are known to play an important role in the catalytic amount of char formation and are known to interact at the C₆ position of cellulose, thereby inhibiting the degradation of cotton fabric.[3,11,57,70-72]

The degradation pathway of dBEP terminates with the final steps of 3 converting to a species which contains a P=O by reacting with water to produce amino-phosphoryldiaminoethane (5). Product 5 will react with another equivalent of itself, where the lone pairs of the secondary amine will attack the P=O to open the ring by cleaving one P—N single bond (6). Typically, aminophosphazenes like anilincyclophosphazenes will eliminate phenylamine during combustion; however, since diaminoethane at the fifth position of dBEP is a cyclic structure, the ring will open.[73,74] Product 6 will then continue to react and release volatiles until a polymerized phospham-like structure (7) is produced.[23] Phosphams (PN₂H)_n are insoluble, infusible, amorphous solids which exhibit thermal and flammability properties.[65,68,75] The secondary amine is protonated by water, which is released during the degradation process, and produces a primary amine. This results in the release of gases such as diethyl-1,2-ethaneamine, ethylamine, methylamine, and ammonia. These gases were observed in the TGA-FTIR spectra and have boiling points of 154°C, 20°C, -6°C, and -33°C, respectively. Diethyl-1,2-ethaneamine was formed via the amine equilibration reaction.[19]

Overall, this supports the suggested degradation pathway that dBEP cleaves to release aromatic, amino, and phosphorous functionalized products that inhibit the production of flammable gases and acts as the protective char barrier for cotton fabric. Product 3 is considered to be a critical component in the FR mechanism of cotton fabric and therefore phosphazene derivatives

containing phosphorus surrounded by three nitrogen atoms may be an effective FR for cotton systems.

4. CONCLUSIONS

The control and treated fabrics and dBEP were used to investigate the thermal degradation pathway of dBEP on cotton fabric. The FTIR reflects the TGA profile of the broad and sharp descent for the control and treated fabrics, respectively. Solid-state NMR, ATR-IR, and TGA support the thermal decomposition of dBEP through structural assignment, functional groups, and onset temperatures. The dBEP partakes in two degradation pathways, (1) decomposition and (2) polymerization, which are collectively attributed to its desirable FR properties. Degradation products of the treated fabric were found in the gas and solid phase. In the gas phase, amino and aromatic gases were released while in the solid phase phosphoric acid and phospham-like products were present. These products are likely to account for the FR behavior such as its high char yield and its high LOI value. The proposed novelty of this phosphazene-based FR is founded on three of the four nitrogen atoms surrounding phosphorus that resembles a phospham-like structure.

Phosphorus surrounded by 3 – 4 nitrogens in a cyclic system may have an important role in providing FR properties. The presence of this moiety may achieve better FR properties and lower additive loading. Future investigations on other phosphazene derivatives on cotton will provide better insight into the flame retardant chemistry of phosphazene. Although this flame retardant has its drawback of not being water-soluble and cross-linked to the fabric, it can be further derivatized to improve both properties.

■ AUTHOR INFORMATION

Corresponding Author

*Email: Michael.easson@ars.usda.gov. Tel.:1-504-286-4493.

Fax: 1-504-286-4390.

Notes

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■ SUPPORTING INFORMATION

A list of tables with ATR-IR, TGA-FTIR, and solid-state NMR values are available free of charge online.

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Figure 1. Structure of dBEP (A) and one glucose unit of cotton fabric (B).

Figure 2. ATR-IR spectra of the control and treated fabrics, and dBEP: full spectra and expanded region.

Figure 3. Flammability results of the control and treated fabrics.

Note: A) 45 degree angle test - all specimens were classified as Class I textiles that do not ignite or the average time of flame spread is 3.5 seconds or more. B. LOI test – 1) < than 21%: flammable; 2) 21 – 26%: slow burning; 3) > 27%: self-extinguishing^[76,77]

Figure 4. TGA thermogram of the control and treated fabrics, and dBEP with char yield and onset temperatures

Figure 5. The evolved gas profile of the control fabric as determined by FTIR.

Figure 6. The evolved gas profile of the treated fabric by FTIR: before (A) and after (B) peaks of gases, and composite (C).

Figure 7. ATR-IR of the control and treated fabrics, and the pyrolyzed treated fabrics at 250, 275, 300, 320, and 375°C full spectrum (A) and expanded region (B).

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Figure 8. Solid-state ^{13}C -TOSS-CP-NMR of the unburned and 320°C fabrics and dBEP.

Scheme 1. The possible thermal degradation mechanism of dBEP on cotton fabric.