

Effect of Metal Ions on the Flame Retardation of Phosphorylated Cotton Cellulose

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This work focuses on the development of durable flame-retarded chemically modified cotton cellulose. Cellulose thiophosphordicarbamidate (CTPC) and its complexes with metals such as chromium and iron have been synthesized and characterized. The thermal oxidative degradation and potential flame retardancy was evaluated from thermogravimetric, differential scanning calorimetry analyses and char yield. From the resulting data of TG curve using Broido method, the activation energies of CTPC and metal complexes ($24\text{--}41\text{ kJ mol}^{-1}$) for decomposition process are found lower than that of cellulose ($165.85\text{ kJ mol}^{-1}$) in static air. It has also been seen that metals have stabilized the CTPC after $350\text{ }^{\circ}\text{C}$ due to cross-linking and aromatization of residue. The FTIR spectra of chars of modified cellulose indicate that catalyzed dehydration takes place. Modified cellulose samples, when heated, give rise to high char yields. The values of ΔH have also been found reduced and spread in wide range of temperature significantly on introducing phosphorus, nitrogen, sulphur and metals in cellulose. This indicates that the combustibility of modified cellulose is reduced.

Key Words: Cellulose thiophosphordicarbamidate, Flame retardant, Cellulose, FTIR, Thermal degradation.

INTRODUCTION

The consumption of textiles used in industry and domestic purposes increases rapidly with the development of society. However it must be acknowledged that it carries with it an increased hazard, since most of the natural and synthetic polymers including cotton are flammable. The field of flame retardancy of polymers has significantly developed and expanded during last two decades. Many papers have been published on the treatment of cotton cellulose with flame retardants¹⁻³ including our earlier studies⁴⁻⁷. The development of new durable flame-retardant systems for cotton are still needed because of difficulty in meeting specific requirements of cotton when flame retarding the fabrics⁸. There has also been major interest in replacing halogenated particularly brominated flame retardants because of

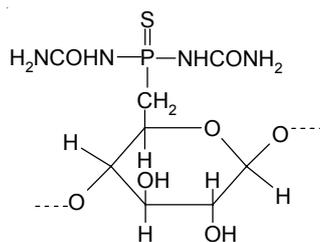
environmental and toxicity issues⁹. Efforts have been strongest in Europe, where waste is generally incinerated. In summary, a satisfactory, durable, flame-retardant treatment for cotton is still a challenge.

These investigations are mainly centered on looking for use of P, N, S and metal synergy to reduce the concentration of bromine used in polymers. Such systematic synergetic studies on flame retardant mechanisms are quite rare. In view of this, cellulose thiophosphordicarbamidate (CTPC) and its metal complexes were synthesized. The kinetics and thermal oxidative degradation of CTPC was studied by thermal analysis (TG and DSC) from ambient temperature to 600 °C in static air and FTIR spectroscopy. The role of formation of char was also studied for flame retardancy. The formation of char has a significant effect on the degradation and flammability because char formation must occur at the expense of other reactions that may limit the amount of fuel available.

EXPERIMENTAL

The compounds used for the present study were cellulose (CDH, India), cellulose thiophosphordicarbamidate (CTPC), complexes of CTPC with Cr(III) and Fe(II).

Synthesis of cellulose thiophosphordicarbamidate: Cellulose thiophosphordicarbamidate was prepared by treating cellulose (0.03 mol of anhydroglucose unit of cellulose) in pyridine (100 mL) with thiophosphoryl chloride (0.045 mol) and guanidine (0.12 mol) at 115 °C for 12 h with constant stirring. The product obtained was filtered, washed with pyridine and then thoroughly washed with distilled water, dried in air then over P₂O₅ *in vacuo* at 80 °C.



Structure of cellulose thiophosphordicarbamidate

Preparation of metal complexes with CTPC: Cr(III) and Fe(II) metal complexes of CTPC were prepared by treating 2-3 g of CTPC with 5 % aqueous solution of chromium(III) sulphate and iron(II) sulphate heptahydrate at room temperature for 72 h with stirring. Each product was filtered, washed with excess warm water until filtrate was free from metal salt and dried first in air then over P₂O₅ *in vacuo* at 80 °C.

Elemental analysis: Elemental analysis of phosphorus by colorimetrically¹⁰, chlorine and sulphur by gravimetrically and nitrogen by Kjeldahl method were carried out. The transition metals analysis was carried out by flame-atomic absorption spectrophotometry using Analytik Jena make Vario 6 spectrophotometer. The results are given in Table-1.

TABLE-1
ELEMENTAL ANALYSIS, UV-VISIBLE ANALYSIS AND DESCRIPTION
OF DSC CURVES OF CELLULOSE, CTPC AND METAL COMPLEXES

| Compound | UV visible peak (nm) | Temperature (°C) | | | Nature of peak | ΔH (J/g) |
|---|-------------------------------|------------------|------|-------|-------------------|---------------------|
| | | Initiation | Max. | Final | | |
| Cellulose | 237 | 275 | 315 | 332 | Exo | 7.65 |
| | 272 | 332 | 345 | 420 | Exo | 1016.60 |
| | 310 | 420 | 482 | 520 | Exo | 1025.20 |
| Cellulose thiophosphor- dicarbamidate (CTPC) | 230 | 180 | 270 | 300 | Exo | 48.28 |
| | 270 | 340 | 380 | 580 | Exo | – |
| (P% = 3.2, N% = 3.8, S% = 3.0, Cl% = 1.1) | 323 | | | | | |
| Cr(III) complex of CTPC | 435* | 250 | 263 | 290 | Exo | 8.32 |
| | 595* | 300 | 412 | 480 | Exo | 2960.60 |
| (P% = 3.0, N% = 3.8, S% = 2.7, Cl% = 0.9, Cr% = 5.2) | | | | | | |
| Fe(II) complex of CTPC | 490* | 210 | 241 | 400 | Exo | 659.80 |
| | | 400 | 420 | 450 | Exo | – |
| | | 480 | 527 | 600 | Exo | 223.86 |
| (P% = 3.1, N% = 3.5 S% = 2.7, Cl% = 1.0, Fe% = 3.3) | | | | | | |

*Peaks in addition to CTPC.

UV-Visible spectral analysis: Reflectance UV-visible spectra of cellulose, CTPC and metal complexes of CTPC were recorded using model 330, UV-S-NIR, Hitachi, Japan. The peaks are given in Table-1.

Thermal analysis: DSC and TG thermograms of all compounds were carried out using Rheometric DSP-SP, TGA-1500 thermal analyzer. The DSC and TG thermograms were recorded in static air from ambient temperature to 600 °C at a heating rate of 10 °C min⁻¹.

FTIR spectroscopy: FTIR spectra of compounds and chars were recorded by the KBr pellet technique using a Shimadzu FTIR-8001 PC, Kyoto, Japan.

Characterization of compounds: Cellulose thiophosphordicarbamidate (CTPC) together with side product chlorodeoxycellulose was formed and confirmed by FTIR characteristic peaks and elemental analysis. Metal complexes of the CTPC were characterized by their reflectance UV-Visible spectra. The Cr(III) complex of the CTPC showed two absorption bands at around 595 and 435 nm which may be due to ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(v_1)$ and ${}^4A_{2g}(F)$

→ ${}^4T_{1g}(v_2)$ transitions, respectively, suggesting an octahedral structure of the complex¹¹. The Fe(II) complex showed one absorption band at 490 nm which may be due to the spin-allowed transition ${}^5T_{2g} \rightarrow {}^6E_g$ for octahedral complex¹².

RESULTS AND DISCUSSION

The residual char yields for cotton cellulose and its derivatives measured at 600 °C are given in Table-2. The data show that the char yield of CTPC (39 %) is more than that of the original cellulose (5.5 %) and is further improved (43-48 %) in case of metal complexes. The existence of P, N, S, Cl elements and metal ions make the char yield much higher than that of original cellulose. This indicates that metal ions can also catalyze the forming of the char. The char retained after burning a polymer is a measure of its flammability¹³ and give insight into the flame performance of the samples.

TABLE-2
TG MASS LOSS AND CHAR YIELD FOR CELLULOSE, CTPC AND METAL COMPLEXES IN AIR

| Compound | T _{10wt%} (°C) | T _{20wt%} (°C) | T _{30wt%} (°C) | T _{40wt%} (°C) | T _{50wt%} (°C) | Char yield at 600 °C |
|---|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|
| Cellulose | 280 | 320 | 330 | 335 | 340 | 5.5 |
| Cellulose thiophosphor- dicarbamidate (CTPC) | 225 | 260 | 300 | 365 | 495 | 39.0 |
| Cr(III)-CTPC | 118 | 240 | 320 | 432 | 525 | 43.0 |
| Fe(II)-CTPC | 112 | 232 | 285 | 465 | – | 48.0 |

The FTIR spectra of the chars of CTPC obtained at different temperatures (upto 350 °C) were recorded. For chars produced at 200 °C, compared to the FTIR spectrum of the original material, the intensity of peaks at 3495 (O-H str.), 2400 (N-H str.), 1490 (C=C and C=N vibrations of pyridine), 1393 (O-H bending), 1283 (P-OH deformation) and 820 cm⁻¹ (P=S str.) decreases and intensity of peak at 1625 cm⁻¹ (C=C str.) increases.

At 250 °C, characteristic peaks of cellulose disappear and a new peak at 1705 cm⁻¹ (C=O str.) appears (shifted from 1715 cm⁻¹) indicating the decomposition process. At 300 °C, all peaks observed at 250 °C remain intact except of shifting of peak 1625 (C=C str.) to 1608 cm⁻¹ (C=C conjugation). At 350 °C, peaks at 2350 (P-H str.), 1705 (C=O str.), 1608 (C=C str.), 1223 (P=O str.), 820 (P=S str.), 762 (P-O str.) and 520 cm⁻¹ (P-S-P str.) are observed suggesting the formation of compounds containing C=O, C=C, P=O and P=S groups.

TG analysis and kinetics

The thermal stability of cotton cellulose, CTPC and metal complexes has been examined using thermogravimetric analysis and the results are given in Table-2. TG data are also shown graphically in Fig. 1. The reported data in Table-2 include the onset temperature ($T_{10wt\%}$) at which 10 % of mass has been lost, the mid-point of degradation ($T_{50wt\%}$), another measure of thermal stability and the fraction that does not volatilize at 600 °C, denoted as char. The data reveal that the onset temperature of degradation has decreased from 280 °C for original cellulose to 225 °C for CTPC and it further decreases by about 100 °C with introduction of metal ions. This is due to catalyzed dehydration in CTPC containing phosphorus because phosphoric acid is released during initial degradation *i.e.*, dephosphorylation takes place. This is the main reason why all P containing samples are effective flame retardants.

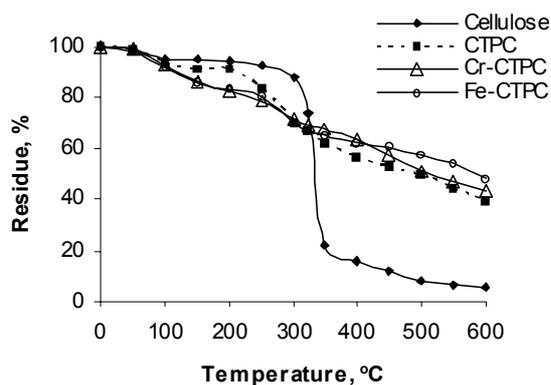


Fig. 1. TGA results in static air: percentage residue of cotton cellulose, CTPC and metal complexes as a function of temperature

The results also indicate that metal ions have further catalyzed the dehydration process. The catalyzed dehydration is considered the first positive steps required for flame retarding the cotton cellulose where hydroxyl groups of cellulose are blocked. The blocking of hydroxyl groups reduces the chances and amount of formation of laevoglucosan the most volatile flammable compound responsible for flame generation¹⁴ while burning of cotton cellulose. Table-2 shows that temperature ($T_{40wt\%}$) before mid-point is increased on phosphorylation and the fraction of non-volatile material is significantly larger. Fig. 2 shows that modification of cellulose has resulted in destabilization of cotton below 300 °C and stabilizes after 350 °C. It is also seen that metals have further destabilized the CTPC below 300 °C and stabilizes after 350 °C. The stabilization takes place due to cross-linking and aromatization of residue¹³ and the metals are also found to have enhanced these processes.

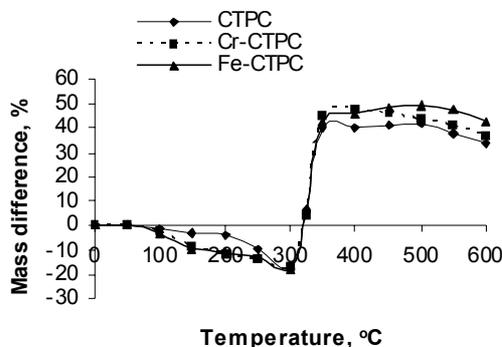


Fig. 2. TGA results in static air: percentage mass difference of CTPC and metal complexes with respect to cotton cellulose as a function of temperature

The kinetic parameters are calculated for decomposition stage from TG data using Broido method¹⁵. The equation used in this method is given below:

$$\ln \left[\ln \left(\frac{1}{y} \right) \right] = -\frac{E_a}{R} \frac{1}{T} + \ln \left[\frac{R}{E_a} \frac{Z}{\beta} T_m^2 \right]$$

where y is the fraction of number of initial molecules not yet decomposed, β is the heating rate, Z is the frequency factor and T_m is the temperature at maximum mass loss rate. Using Broido equation, plots of $\ln[\ln(1/y)]$ vs. $1/T$ for decomposition stage of thermal degradation of cellulose, CTPC and metal complexes are plotted. The activation energies and frequency factors calculated from the slopes and intercepts, respectively, of these plots are given in Table-3. The data indicate that the activation energies during decomposition stage are low for modified cellulose samples (24-41 kJ mol⁻¹) compared with the original cellulose (165.85 kJ mol⁻¹) because of catalization of degradation. The thermodynamic quantities such as entropy, enthalpy and free energy of activation were calculated using transition state theory at the respective T_m , the temperature at maximum mass loss rate, for the second (decomposition) step of degradation of cellulose and its derivatives are given in Table-3. The cellulose derivatives show variation in the values of entropy of activation (-227 to -265 J K⁻¹ mol⁻¹) but this variation is compensated by a change in values of enthalpy of activation (19-33 kJ mol⁻¹) leading to the almost constant values of free energy of activation (165-174 kJ mol⁻¹). This indicates that basic step¹⁶ involved in decomposition stage does not change on modification of cotton cellulose.

TABLE-3
KINETIC AND THERMODYNAMIC PARAMETERS OF
DECOMPOSITION PROCESS OF CELLULOSE, CTPC AND METAL
COMPLEXES IN AIR

| Compound | Temperatu re range (°C) | T _m (°C) | E _a (kJ mol ⁻¹) | Z (s ⁻¹) | ΔS* (J K ⁻¹ mol ⁻¹) | ΔH* (kJ mol ⁻¹) | ΔG* (kJ mol ⁻¹) |
|---|-------------------------------|---------------------|---|-----------------------|---|--------------------------------|--------------------------------|
| Cellulose | 300-355 | 330 | 165.85 | 2.63×10 ¹² | -21.30 | 160.83 | 173.67 |
| Cellulose thiophosphor- dicarbamidate (CTPC) | 270-340 | 300 | 40.94 | 4.49×10 ¹ | -227.01 | 32.17 | 166.24 |
| Cr(III) complex of CTPC | 250-400 | 325 | 24.21 | 5.54×10 ⁻¹ | -264.19 | 19.81 | 173.83 |
| Fe(II) complex of CTPC | 230-370 | 310 | 30.30 | 5.51 | -244.45 | 25.53 | 165.59 |

DSC analysis

From the DSC curves (Fig. 3) of samples obtained in static air upto 600 °C, peak temperatures alongwith the values of enthalpy change were measured and are given in Table-1. DSC curve of cellulose shows two major exothermic peaks at 345 and 482 °C with ΔH values 1016.6 and 1025.2 J/g, respectively. First peak may be attributed to decomposition and rearrangement of products of cellulose leading to the formation of laevoglucosan the major volatile product and the second peak may be attributed to the oxidation of volatile and charred products. In case of CTPC, two major exothermic peaks at 270 °C (ΔH = 48.28 J/g) and 380 °C appear due to decomposition, oxidation and aromatic cyclization of charred residue. Cr complex of CTPC shows one large exothermic peak at temperature 412 °C (ΔH = 2960.60 J/g) which could not be resolved due to concurrence of various reactions. Fe complex shows a clear exothermic peak at 241 °C with ΔH value 659.8 J/g due to catalyzed dehydration and decomposition of the sample. It gives another exothermic peak at higher temperature 527 °C with ΔH value 223.86 J/g which may be attributed to decomposition of polythiophosphoric acid. DSC peaks are supported by mass loss indicated by TG curves.

DSC curves of CTPC and its metal complexes show that initial peaks are shifted to lower temperature because of catalyzed dehydration and on introduction of metal ions last exotherm peaks shifted to higher temperature and become broader because of stabilization by cross-linking and aromatization of residue products and polymerization of released phosphoric

acid¹⁷. All these indicate that metal ions have changed the degradation process. Table-1 also reveals that the values of enthalpy change have also been found to be spread over a wide range of temperature during degradation of modified cellulose compounds in comparison to original cellulose. This indicates that the combustibility of modified cellulose is reduced.

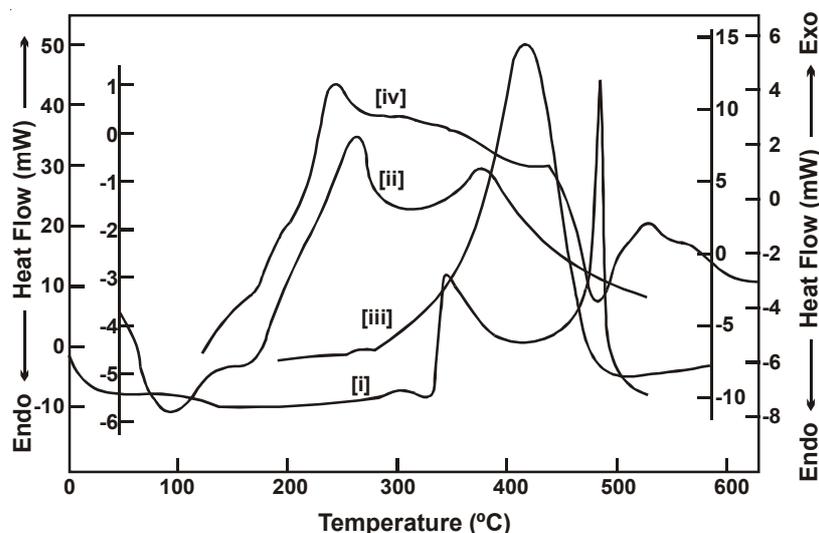


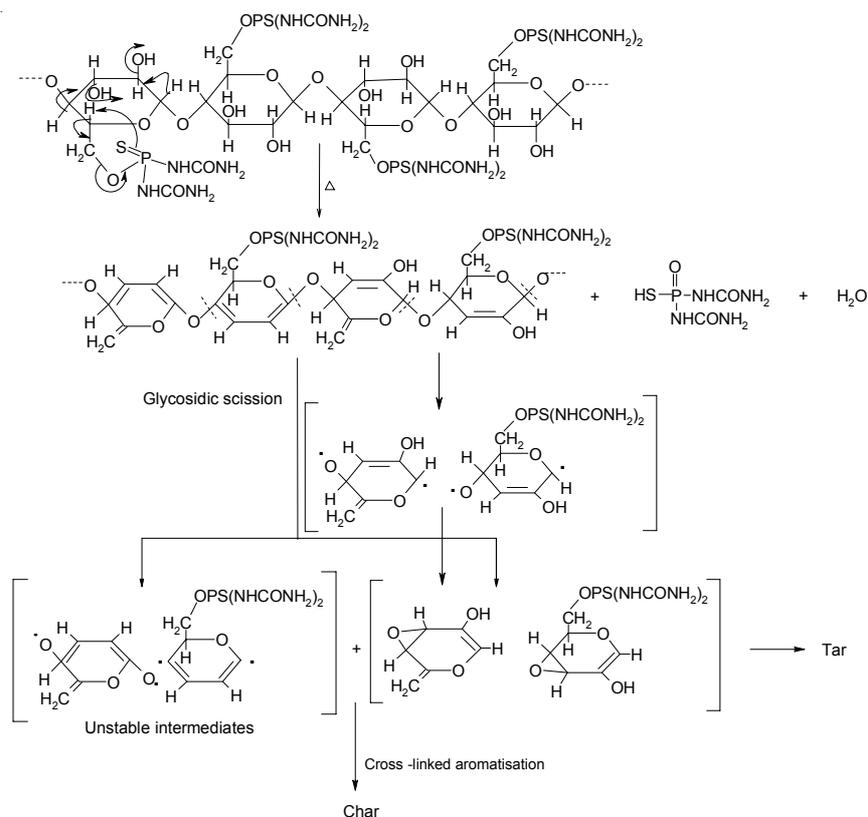
Fig. 3. DSC curves of [i] cotton cellulose, [ii] CTPC, [iii] Cr-CTPC complex and [iv] Fe=CTPC complex in static air

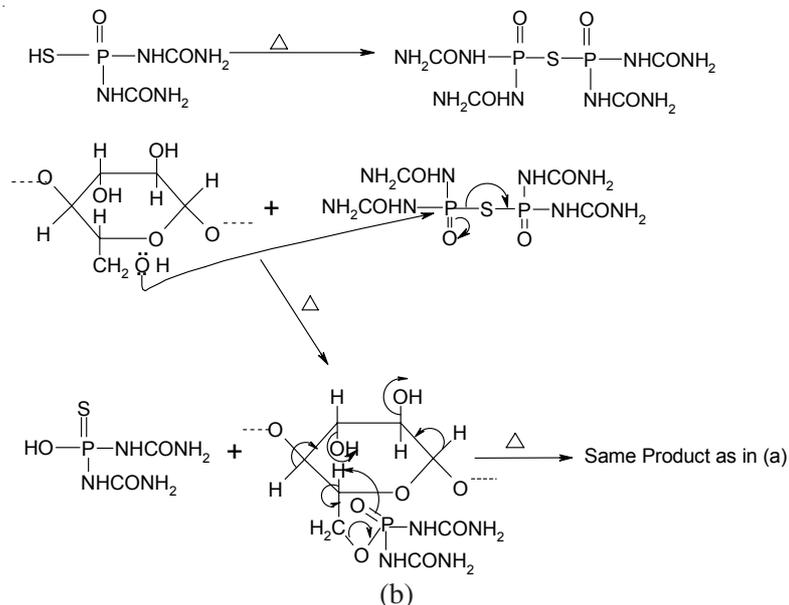
Flame retardancy mechanism for CTPC and metal complexes

The most conventional mechanism for phosphorus flame retardancy in cotton cellulose is considered to occur in the condensed phase. Thermal degradation of cellulose thiophosphordicarbamidate starts with the generation of thiophosphoric acid dicarbamide. This acid then alters the decomposition of the substrate to such an extent that the primary decomposition products are changed by dehydration from laevoglucosan and other flammable products to carbonaceous char¹⁸. Thiophosphoric acid dicarbamide on further heating may generate dimer of it. In addition, dehydration can also occur by a single step acid catalyzed elimination of water. The acid-catalyzed dehydration of cellulose at primary hydroxyl groups results in formation of an exocyclic methylene, whereas at secondary hydroxyl groups, it results in endocyclic double bond.

At high temperature, thiophosphoric acid polymerized, which is more effective in catalyzing the dehydration. It can react with cellulose moiety which then breaks down to give water, thiophosphoric acid and unsatur-

ated cellulose analogue and eventually char by repetition of these steps. Chlorodeoxycellulose is also formed together with CTPC; consequently the mechanism of degradation is also affected by chlorine. The released hydrogen chloride then catalyzes a series of heterolytic and homolytic cleavage of the substituents on the carbon chain of the condensation products which give a carbonaceous char³. A similar mechanism has been shown by Shafizadeh *et al.*¹⁹. In the case of metal complexes of CTPC, the first step is removal of octahedral complexes of CTPC from cellulose moiety and decomposes to give a metal thiophosphate and thiophosphoric acid. These products can polymerize to form poly-metal thiophosphate and polythiophosphoric acid, which further catalyze the dehydration. The effect of metal chlorides as Lewis acids formed during degradation by the reaction of hydrogen chloride with metal ions is similar to that of hydrogen chloride in promoting the dehydration, condensation and charring. Thermal degradation mechanism of cellulose thiophosphordicarbamate leading to char formation can be depicted as in **Scheme-Ia-b**.





Scheme-Ia-b Thermal degradation mechanism of CTPC leading to char formation

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