

## Preparation and Thermal Performance of Fullerene-Based Lead Salt

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C<sub>60</sub> is widely investigated because of its unique structure. But its applications in solid propellant seem to be relatively neglected. C<sub>60</sub> has more outstanding features than carbon black which is widely used as a catalyst ingredient of solid propellant. To combine the advantages of fullerene and lead salts, another good composite in propellant catalysts, we synthesized a kind of fullerene phenylalanine lead salt (FPL) and explored its thermal performances by differential thermal analysis (DTA) and thermogravimetry analysis (TGA). The results show it undergoes four exothermic processes started from 408 K. Combined TGA and X-ray diffractometer (XRD), the decomposition mechanism of FPL was derived by TG-IR and comparing IR spectra of FPL and its residues after burned to 327 °C, 376 °C and 424 °C, respectively. Effect of FPL on the decomposition characteristic of hexogen (RDX), a type of explosive in propellant, has been investigated using DTA at different heating rate, which shows the decomposition temperatures of the explosive are all reduced by more than 20 K. The corresponding activation energy ( $E_a$ ) is decreased by 30 kJ·mol<sup>-1</sup>. So FPL has potential application as a combustion catalyst in solid propellant.

**Key Words :** Fullerene phenylalanine lead salt, Thermal decomposition, Combustion catalyst, Solid propellant

### Introduction

Fullerenes are a kind of three-dimensional molecules made up of pure carbon. Because of its availability and unique structure, C<sub>60</sub> is widely studied as a star molecule of fullerene family in areas such as energy, materials, optics and biopharmaceuticals. Fullerene-related energy researches are mainly as an electron acceptor material in solar cells because of its fine electrophilicity. But study of fullerene as an additive in solid propellant has rarely been concerned.

To find a kind of recyclable solid propellant with high energy, high burning speed, high strength and low sensitivity is the goal in solid rocket propellant development. The combustion catalyst can effectively regulate the combustion performance of solid rocket propellant.<sup>1</sup> To improve the combustion performance of the propellant, the main method is to seek a combustion catalyst with excellent performance under the premise of not changing current propellant ingredients.

Currently, most of combustion catalysts are the ternary "lead-copper-carbon" combination which consists of lead salt, copper salt and carbon black. As the outstanding representative in fullerene family, C<sub>60</sub> has the crystal formation enthalpy of 2280 kJ·mol<sup>-1</sup>, and it is very stable at room temperature. Crystals of C<sub>60</sub> heated at 1260 K for more than 10 min decomposed into amorphous carbon without losing their faceted morphology.<sup>2</sup> It is reported that if C<sub>60</sub> in place of carbon black in the combustion catalyst system, the burning rate and efficiency of solid propellant can be improved.<sup>3-5</sup> Lead salt was the platform catalyst that is the first to be found and put into use. Lead salt can not only increase the burning rate of double-base propellant but also produce their

platform effect. And the platform effect has not been transcended by other combustion catalysts so far.<sup>6-12</sup> Researchers have proved that carbon material can significantly enhance the catalytic effect of lead salt when it used mixed with lead.

Nowadays, lead salt related catalysts are mainly inert or including nitro groups if energetic. But the sensitivity must be taken into account in the latter. Based on the current research status of combustion catalyst, the preparation of FPL was put forward to derive a new type of combustion catalyst. As a new combustion catalyst, we inferred that FPL would have excellent comprehensive properties, because it combined the advantages of fullerene and lead salts. At the same time, the mixture of FPL and the other ingredients of propellant would have a better uniformity than the mixture of carbon material, metal salt and the other ingredients of propellant. Of course, catalytic composition of carbon material and metal salt all can be provided.

In our previous work, some *N*-nitrophenylfulleropyrrolidine derivatives, fullerenes glycine lead/copper salts, fullerenes ethylenediamine lead/copper salts and fullerenes itaconic acid copolymer lead/copper salts were synthesized. Exploratory research results show that they all have certain catalytic effect on double-base propellants.<sup>13-16</sup> Here we synthesized a kind of FPL, explored its thermal performance and derived its decomposition mechanism. The effects of FPL on a main ingredient of propellant, RDX, were also preliminarily explored.

### Experimental Section

**Materials and Instruments.** C<sub>60</sub> was prepared by modi-

fied combustion method in our group<sup>17</sup> and the purity of C<sub>60</sub> is 99.9% after refinement by HPLC. All other reagents purchased from commercial suppliers were of analytical purity and used without further purification. FT-IR spectra were obtained on America Nicolet 800 FT-IR spectrophotometer in the region of 400-4000 cm<sup>-1</sup>. UV-vis absorption spectra were performed on America Unicam UV-2102PCS in the range of 200-600 nm. The XPS spectra were obtained with America Thermo VG250 X-ray photoelectron spectrometer using Al K $\alpha$  radiation. DTA and TGA of FPL were carried out on America SDT Q600 synchronous thermal analyzer. XRD analysis was performed on Netherlands X'Pert PRO X-ray diffractometer. The decomposition behaviour of FPL was studied by continuous monitoring with TGA (Q500, TA Instruments Corporation, USA) coupled to infrared spectrometry (Nicolet 6700, Nicolet Instruments Corporation, USA) (TG-IR). The catalytic performance studying of FPL to RDX was performed with Beijing WCR-1B Micro-computer differential thermal analyzer.

**Preparation of FPL.** Fullerene phenylalanine (FP) (100.0 mg) which was prepared according to the method<sup>18</sup> was dissolved in 10 mL water, then the pH of FP water solution was adjusted to 6.96 using 1 mol/L HNO<sub>3</sub>. And the aqueous solution of Pb(NO<sub>3</sub>)<sub>2</sub> (5 mL, 2 mol/L) was added. Then the mixture was stirred at 30 °C for 3 h and a yellow precipitate appeared. After filtration, the precipitate was washed with 10 mL water for five times to remove unreacted Pb(NO<sub>3</sub>)<sub>2</sub>. The product was dried under vacuum to give FPL (152.6 mg). The synthesis route was shown in Scheme 1.

**Pyrolysis Experiment.** Thermal decomposition experiment of FPL (2.22 mg) was performed using SDT Q600 thermal analysis system with synchronous thermal analyzer in dynamic air atmosphere (100 mL/min). Experiment was conducted from room temperature to 650 °C with heating rate of 10 K/min. XRD and TG-IR were applied to further determine the decomposition behaviour of FPL. The operating conditions of the FT-IR were as follows: frequency range was 4000-670 cm<sup>-1</sup>, TG test was carried in air atmosphere in the temperature range from room temperature to above 700 °C at a heating rate of 10 °C/min.

**Catalytic Activity Test.** The dynamic experiments of RDX before and after adding FPL were performed on WCR-1B differential thermal analyzer in the temperature range from room temperature to 350 °C under air atmosphere. The

tests were carried out at four different heating rates: 2.5, 5, 10 and 20 K/min. The sample weight of RDX was 3.0 mg alone and the added FPL was 3.0 mg to make the RDX-FPL mass ratio be 1:1.

## Results and Discussion

Fullerene-based amino acids have always been explored for their biomedical properties. Here we synthesized FP in order to get its lead salt. FP was synthesized and its IR spectrum is similar to the literature.<sup>18</sup> Mass analysis was applied to get its molecular weight. But only the *m/z*, 735.35 peak of C<sub>60</sub>-N (M<sup>+</sup>) was observed. Therefore, it only indicate that FP is derived by MS. And the determination of the number of functional groups by this method is not possible. FPL was a yellow precipitate in water obtained by making FP reacted with Pb(NO<sub>3</sub>)<sub>2</sub>, while there was no water-insoluble matters observed when phenylalanine reacted with Pb(NO<sub>3</sub>)<sub>2</sub> in the same conditions. So we think fullerene-based lead salt was formed. The IR spectra of FP and FPL are compared in Figure 1. The absorption around 575 cm<sup>-1</sup> is attributed to the vibration of fullerene skeleton which is obvious in Figure 1(a). That peak become relatively weak but also can figure out in Figure 1(b). IR active modes for C-N stretch occurs at 1062 cm<sup>-1</sup>. When Pb replaces the

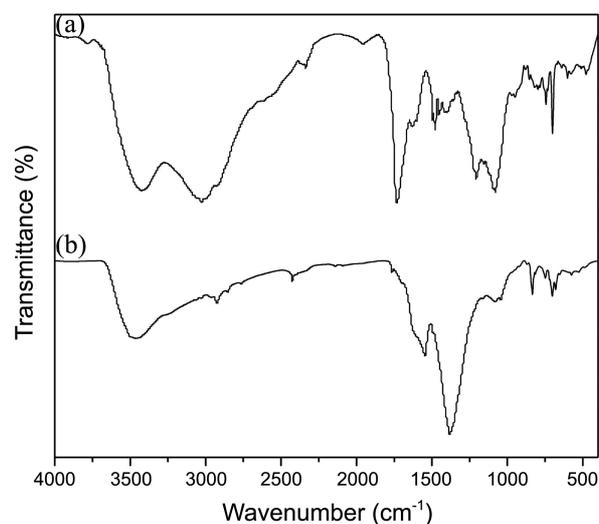
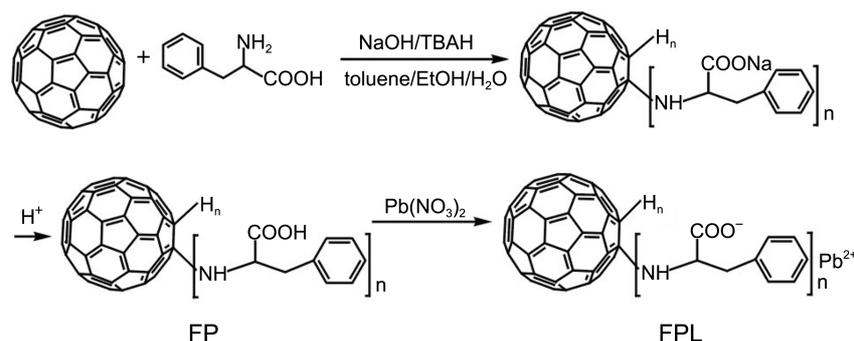


Figure 1. IR spectra of (a) FP and (b) FPL.



Scheme 1. The synthesis of FPL.

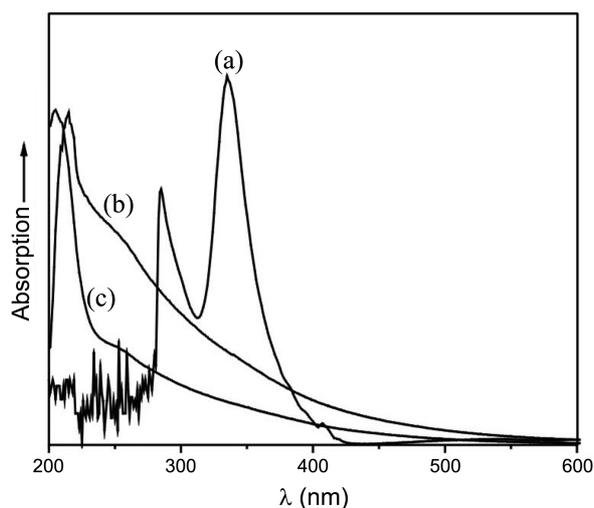


Figure 2. UV-vis spectra of (a) Fullerene, (b) FP and (c) FPL.

hydrogen on carboxylic acid. The peaks at 3000 and 1627  $\text{cm}^{-1}$  which belong to hydroxyl vibration are disappeared in FPL, instead a strong peak at about 1384  $\text{cm}^{-1}$  arises because of vibration of carboxylates. These results indicate that the hydrogen in hydroxyl is replaced by Pb after FP reacts with  $\text{Pb}(\text{NO}_3)_2$ . The absorptions around 1547 and 1384  $\text{cm}^{-1}$  are assigned to asymmetric and symmetric  $-\text{COO}^-$  stretching modes respectively.<sup>19,20</sup> And the absorption around 709  $\text{cm}^{-1}$  is attributed to the bending vibration of C-H on benzene ring (Figure 1(b)).

UV-Vis spectra of FP and FPL are compared with that of parent  $\text{C}_{60}$  (Figure 2). The characteristic peaks of  $\text{C}_{60}$  are at 285, 335 and 407 nm (Figure 2(a)), which suggests that  $\text{C}_{60}$  has a highly symmetrical  $\pi$ -conjugated electronic structure system.<sup>16</sup> The three characteristic peaks of  $\text{C}_{60}$  are all disappeared in FP and FPL due to poly-addition of fullerene. The peaks of the absorption maxima of FP and FPL appears in around 215 and 205 nm respectively. Compared with those of FP, the maximum absorption of FPL showed a little

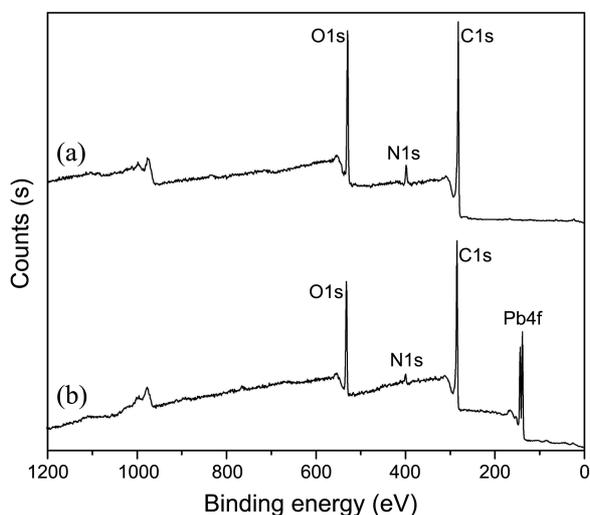


Figure 3. XPS survey spectra (a) FP and (b) FPL.

Table 1. XPS spectra data of FP and FPL

Product	Binding Energy/eV			
	O1s	C1s	N1s	Pb4f
FP	529.54	281.95	398.80	–
FPL	529.30	282.14	396.95	136.13

blue shift because of the replacement of H by Pb.

According to the existing literature data, the X-ray photoelectron survey spectra of FPL indicated the presence of four distinct peaks due to lead, carbon, nitrogen and oxygen (Figure 3). The XPS spectra data of FP and FPL are listed in Table 1. The peak with the binding energy of 136.13 eV can be ascribed to  $\text{Pb4f}$ .<sup>21</sup> The binding energy of C1s is 282.14 eV, compared with FP, XPS C1s spectra of FPL showed a rise, the peaks with higher binding energies can be attributed to the decrease of carbon's outer electron density, its decrease is caused by the moving of the carbon atoms electron clouds to the oxygen atom when oxygen atom formed coordinate bond with lead atom. N1s with a binding energy of 396.95 eV was observed, the position shows little variation with the decrease in binding energy, the cause may be that nitrogen atom formed electron cloud with ionized carboxylic acid root. The binding energy of O1s is 529.30 eV, showed a lower compared with the O1s of FP, due to the oxygen atom negatively charged by forming big  $\pi$  bond with carbon atom.<sup>22-24</sup> The XPS analysis of FPL illustrated a replacement of H to lead.

The DTA and TG-DTG curves of FPL are shown in Figure 4 and Figure 5. In this research, when FPL was heated in air atmosphere during DTA, it can be found that FPL has four exothermic peaks on DTA curves, which indicated that thermal decomposition of FPL occurs mainly in four steps. FPL is thermally stable until to  $\sim 135$  °C. The second transition zone is detected at 328.97-379.01 °C. The third reaction is identified at 379.01-425.98 °C. And the last

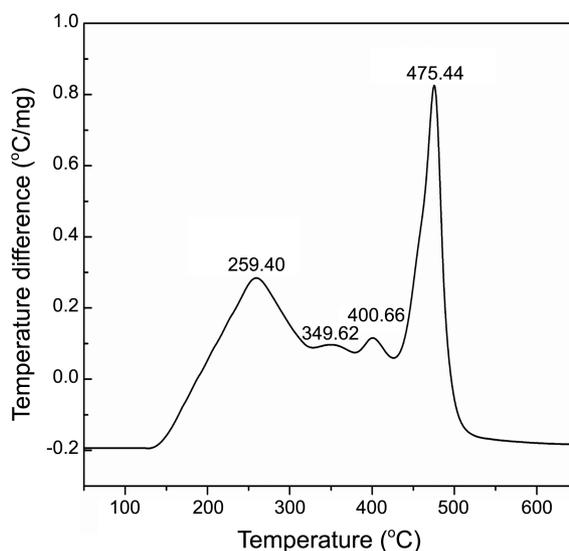


Figure 4. DTA curve of FPL.

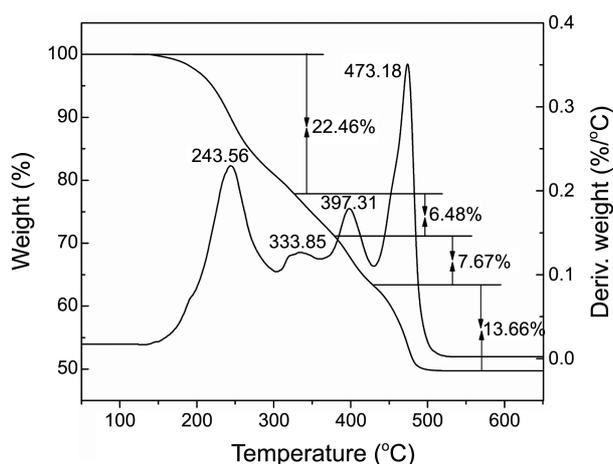


Figure 5. TG-DTG curves of FPL.

decomposition reaction completely finishes until at 528.80 °C, and the values of  $T_p$  are presented at 259.40, 349.62, 400.66 and 475.44 °C respectively.

TG-DTG curves indicated that thermal decomposition occurs in four steps for FPL, too. At the same time, it can be seen that the mass lose process finishes completely at 528.80 °C. As the temperature continue to increases, the residue are thermally stable, and the mass lose rate observed of the four processes were 22.46%, 6.48%, 7.67% and 13.66%, respectively. So the residue rate of FPL after burning reaches to 49.73%.

Nevertheless, the final residue can be confirmed by XRD. To illustrate the composition of the residue of FPL after being heated to 530 °C in muffle furnace, XRD analysis was explored. The XRD pattern of the residue of FPL after heated to 530 °C is reported in Figure 6. Compared with reference code (PbO, JCPDS 00-038-1477), the result demonstrates that the residue is pure PbO. By calculation, the ratio of lead in FPL is 46.16% or so. And the addition number of phenylalanine is 8 or 9 in FP given the test error. So is it in FPL.

Three-dimensional FT-IR spectra of FPL is presented in

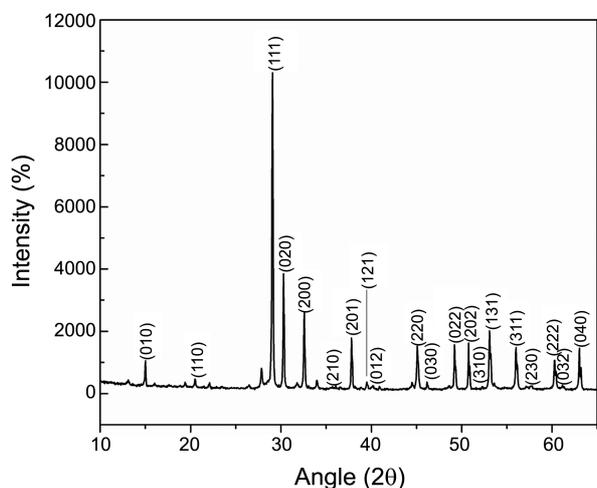


Figure 6. XRD pattern of the residue of FPL after heated to 530 °C.

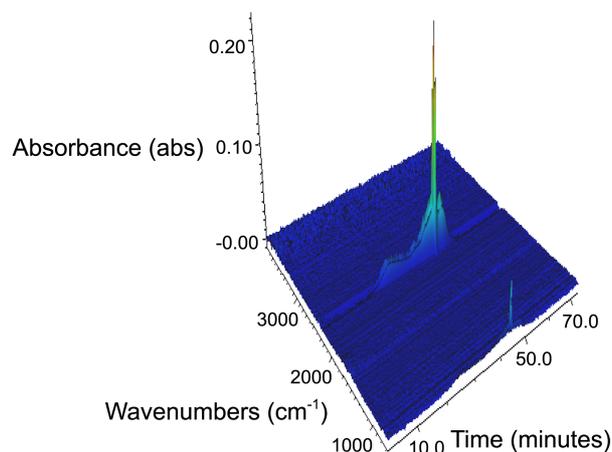


Figure 7. Three-dimensional FT-IR spectra of FPL.

Figure 7. Gas infrared spectra at different temperatures for FPL under air are presented in Figure 8. Figure 7 and Figure 8 show  $\text{CO}_2$  peaks at around 2363  $\text{cm}^{-1}$ , 2313  $\text{cm}^{-1}$  and 670  $\text{cm}^{-1}$  in the temperature range of about 135 to 528.80 °C and water peaks at around 3714  $\text{cm}^{-1}$ , 3621  $\text{cm}^{-1}$  and 1565  $\text{cm}^{-1}$  in the temperature range of about 135 to 379.01 °C.<sup>25,26</sup>

XRD and TG-IR experiments show that the main products of FPL decomposition were  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{PbO}$ . In the entire process of FPL decomposition,  $\text{CO}_2$  generated reaction have been performed. However, water is generated only in the first two steps. And the final product of FPL decomposition is pure  $\text{PbO}$ .

To further explore what actually happened during the four exothermic processes, the residue of FPL in TGA test at the end of every exothermic process was collected at 327 °C, 376 °C and 424 °C, respectively. Their FT-IR spectra com-

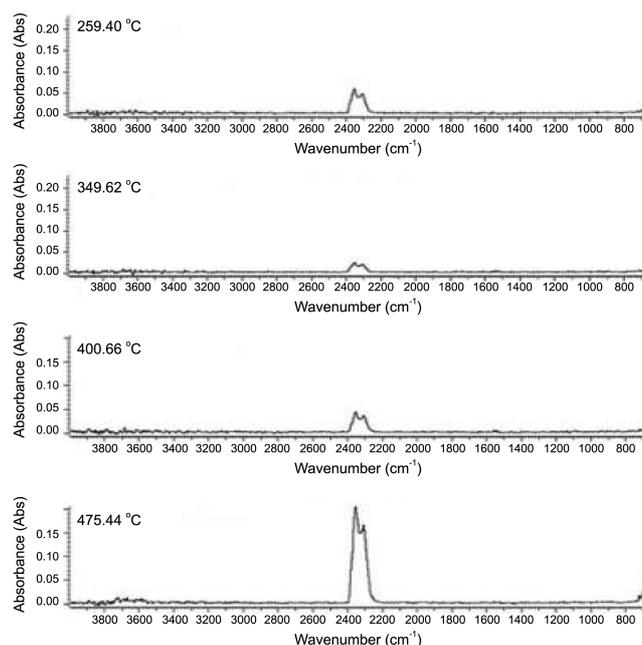
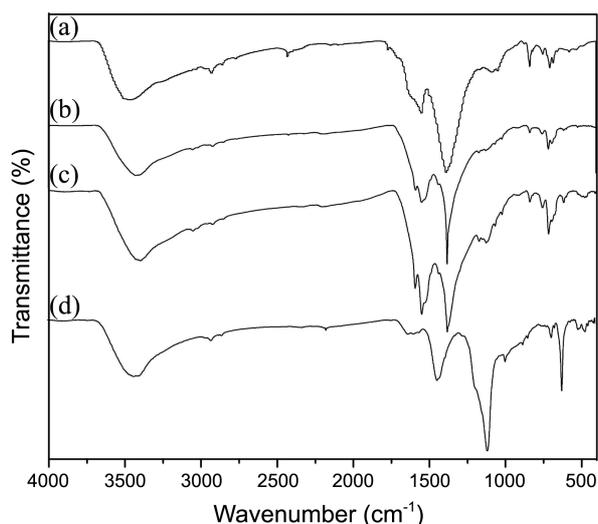


Figure 8. Gas infrared spectra at different temperatures for FPL under air.

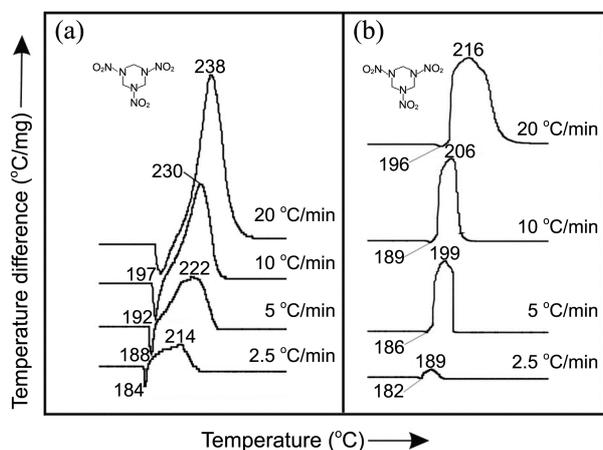


**Figure 9.** IR spectra of (a) FPL and its residues after burned to (b) 327 °C, (c) 376 °C and (d) 424 °C, respectively.

pared with that of FPL are listed in Figure 9.

IR characteristic absorption peaks of the asymmetric and symmetric  $\text{-COO}^-$  stretching around  $1540\text{ cm}^{-1}$  and  $1370\text{ cm}^{-1}$  of FPL are still exist in Figure 9(b) and Figure 9(c), which indicates that  $\text{-COO}^-$  are still kept when FPL is heated to 327 °C and 376 °C. After heated to 424 °C, they are all disappeared, that is, decarboxylation is occurred. The absorption bands around  $1429$  and  $1186\text{ cm}^{-1}$  are attributed to the vibration of fullerene skeleton, bands at  $1108\text{ cm}^{-1}$  shows the C-N stretching vibration (Figure 9(d)). Combined with XRD, TG and TG-IR, therefore, the first two steps reaction conformed the decomposition of benzene ring and  $\text{-CH}_2\text{CH}$  respectively. The third reaction is the decomposition of  $\text{-COO}^-$ . The last reaction is due to the decomposition of  $\text{C}_{60}\text{-N}$ .

The effects of FPL on RDX decomposition were explored by DTA. Figure 10 shows the DTA curves of RDX in the (a) absence and (b) presence of FPL at different heating rates. It can be seen the decomposition of RDX is reduced by more



**Figure 10.** DTA curves of RDX in the (a) absence and (b) presence of FPL at different heating rates.

**Table 2.** The kinetic parameters of RDX before and after adding FPL

Product	Kinetic parameters				
	kissinger method			Ozawa method	
	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	$\ln(A/\text{s}^{-1})$	$R^2$	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	$R^2$
RDX	171.77	40.84	0.9988	171.80	0.9987
RDX/FPL	140.78	34.95	0.9973	141.64	0.9975

than 20 K at diverse heating rate.

The kinetic parameters were calculated by (1) Kissinger equation and (2) Ozawa equation, the expressions of which are given below respectively:

$$\ln[\beta/T_p^2] = \ln[AR/E_a] - [E_a/RT_p] \quad (1)$$

$$\lg\beta = C - 0.4567E_a/RT_p \quad (2)$$

Where  $\beta$  is heating rate,  $T_p$  is the peak temperature of heat release,  $A$  is pre-exponential factor,  $E_a$  is activation energy,  $C = \lg[AE_a/RG(\alpha)] - 2.315$  and  $R$  is gas constant.<sup>27,28</sup>

When the experiment data are substituted in the equations, linear correlation of  $\ln[\beta/T_p^2]$  versus  $1/T_p$  and  $\lg\beta$  versus  $1/T_p$  are fairly well, which means the two methods are both suitable for this system. The corresponding decomposition activation energies calculated by these two methods are listed in Table 2. From the table we can see the  $E_a$  decreased by about  $30\text{ kJ}\cdot\text{mol}^{-1}$  when FPL was added in RDX, which means that the thermal decomposition rate of RDX was speeded up and it is beneficial to improve the burning performance of propellant.

## Conclusion

We have synthesized a kind of fullerene-based lead salt, FPL, and its thermal characters are explored by DTA and TGA. Its start decomposition temperature is at about 408 K and goes through four exothermic processes to have only  $\text{PbO}$  left. Combined with TGA, the decomposition mechanism of FPL was derived by XRD, TG-IR and IR spectra of FPL and its residues after burned to 327 °C, 376 °C and 424 °C, respectively. Preliminary work of the thermal effect of FPL on RDX, a solid propellant ingredient, has been studied by kinetic analysis through DTA at different heating rates. According to the results and calculations, we found the activation energy of RDX was reduced by  $30\text{ kJ}\cdot\text{mol}^{-1}$  or so when FPL was added into it, which indicates that FPL has a certain catalytic effect on RDX combustion.

Further work of FPL and other types of fullerene-amino acid salts on combustion effect of solid propellant is underway. If all results are positive, fullerene-based lead salts will have potential application as catalysts in solid propellants. As the pilot scale test of  $\text{C}_{60}$  production is successful in our group,<sup>12</sup> which means industry produce in 100 kilograms per year is feasible, we hope fullerene-related material can really be used in solid propellant field to improve its combustion

performance for energy conservation.

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