

用 T-jump/FTIR 研究 MnCP、NiCP 和 PbCP 的快速热分解

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关键词: 高氯酸; 碳酰肼配合物; 快速热分解; T-jump/FTIR

中图分类号: TQ564.4

文献标识码: A

文章编号: 1001-4861(2005)01-0113-04

The Flash Pyrolysis of $[\text{Mn}(\text{CHZ})_3](\text{ClO}_4)_2$ (MnCP), $[\text{Ni}(\text{CHZ})_3](\text{ClO}_4)_2$ (NiCP) and $[\text{Pb}(\text{CHZ})_3](\text{ClO}_4)_2$ (PbCP) by T-jump/FTIR Spectroscopy

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Abstract: $[\text{Mn}(\text{CHZ})_3](\text{ClO}_4)_2$ (MnCP), $[\text{Ni}(\text{CHZ})_3](\text{ClO}_4)_2$ (NiCP) and $[\text{Pb}(\text{CHZ})_3](\text{ClO}_4)_2$ (PbCP) (CHZ=Carbohydrazide) were flash pyrolyzed at different temperatures under the set pressure by T-jump/FTIR spectroscopy. The results show that twelve gas products obtained during the flash pyrolysis process of the three complexes were CO_2 , CO, HCl, HCN, NH_3 , NO_2 , N_2O , NO, HNCO, HONO, $\text{H}_2\text{C}=\text{O}$ and H_2O , of which CO_2 , HCN and HCl were the main gas products and CO_2 was the most novel product. NH_3 was oxidized to NO_2 , N_2O and H_2O . At least some of the N_2O might result from this reaction. Additionally, the effect of temperature on the gas products is discussed and the concentration-time change curves of the main gas products are given.

Key words: perchlorate; carbohydrazide complex; rapid thermolysis; T-jump/FTIR

0 Introduction

Carbohydrazide is a hydrazine derivative with white crystal of strong reducing behaviors. Because it has many coordination atoms (four nitrogen atoms and one oxygen atom), carbohydrazide can, therefore, be used as multidentate ligand. Its coordination compound is widely used in the field of medicine, petroleum, national defense and energetic materials and so on^[1]. In the field of energetic materials, carbohydrazide has many peculiar applications. It can be used not only as an ingredient of propellants^[2,3] but also can be combined in energetic explosives^[4,5].

In recent years, carbohydrazide energetic coordination compounds have received extensive attentions due to their potential properties such as good fluidity

and lower sensitivities^[6~8], therein the coordination compounds of carbohydrazide and perchlorate show good explosive properties. $[\text{Cd}(\text{CHZ})_3](\text{ClO}_4)_2$ has already been used as primary explosive to bring in satisfactory social benefit and economical benefit in industry. We have already studied the thermal decomposition mechanisms of these organic compounds by using DSC, TG-DTG and FTIR technologies^[7,9]. In order to investigate the significant chemistry that occurs in the surface layer, the flash pyrolysis properties of $[\text{Mn}(\text{CHZ})_3](\text{ClO}_4)_2$ (MnCP), $[\text{Ni}(\text{CHZ})_3](\text{ClO}_4)_2$ (NiCP) and $[\text{Pb}(\text{CHZ})_3](\text{ClO}_4)_2$ (PbCP) were studied with T-jump technology^[10,11] and rapid-scan spectroscopy under different temperatures and different pressures. The gas products during the flash pyrolysis were identified

收稿日期: 2004-05-12. 收修改稿日期: 2004-08-07.

国家自然科学基金资助项目(No.20471008), 北京理工大学基础研究基金(No.BIT-UBF-200302B01).

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and the concentration-time change curves of the main gas products are given.

1 Experimental

1.1 Reagents and apparatus

Samples of MnCP, NiCP and PbCP were self-synthesized according to the previous methods^[9] and further purification was also attempted in several instances. The IR spectra were recorded on a Nicolet 20SXB FTIR spectrometer with an MCT detector. The flash pyrolysis of the samples was examined by T-jump FTIR spectroscopy^[10,11].

The data processing was accomplished by using the Matlab procedure^[12]. We can, thus, get the gas products during the flash pyrolysis process and suggest the concentration-time change curves of the main gas products simultaneously.

1.2 T-jump/FTIR spectroscopy

Flash pyrolysis of the three complexes was characterized by using T-jump/FTIR spectroscopy^[10]. The sample was dried in vacuum for 24 h prior to use. Approximately 0.5 mg of sample was thinly spread on the center of the Pt ribbon filament housed in a gas-tight IR cell^[10]. The cell was flushed with Ar gas and the pressure was adjusted to 0.1 MPa. The filament was heated by a power control unit to the set temperature. The true temperature of the Pt filament with different applied power values was determined by calibration with compounds having standard melting points. A block diagram of the T-jump/FTIR system is shown in Fig.1.

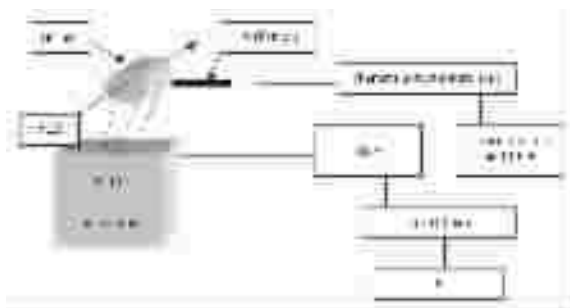


Fig.1 A block diagram of the T-jump/FTIR spectroscopy system

The Pt filament is inserted through the cell wall as shown.

Control over the filament was achieved by rapidly sensing its resistance. Endothermicity and exothermicity of the sample were detected by monitoring the control voltage required to maintain constant resistance. The different control voltage was obtained by

subtracting the voltage of the filament without sample from the voltage when the sample was present.

Because of the small mass of the sample, its temperature is relatively uniform. The sample and the filament form a reaction zone containing the gas and condensed phases in close contact with the heat source. From the point view of the chemistry of the heterophase surface, this condition qualitatively resembles a surface during combustion. Instead of forming a flame, the decomposition gas products were quenched by the cool Ar atmosphere. They rise by convection into the IR beam, which is about 3 mm above the sample surface. The complete IR spectrum of the thermally quenched gas products was collected at 0.2 s intervals with 4 cm⁻¹ resolution.

2 Results and discussion

The control voltage trace of MnCP under the experimental circumstance is shown in Fig.2. It can be seen that the inflection is positive for MnCP at first, indicating that an endothermic process occurs at the initial flash pyrolysis process. Then there exist two successive intense negative inflections, which indicates that MnCP sends out heat sharply in the exothermic decomposition processes. As shown in Fig. 3, the inflection is also positive for NiCP at first, its initial decomposition process is endothermic melting as well. Compared with MnCP, its endothermic melting process is much more abrupt. Furthermore, there is only one intense negative inflection. The decomposition process of PbCP is similar to NiCP in general (shown in Fig.4), but the exothermic process occurs later (nearly at the end of the decomposition process).

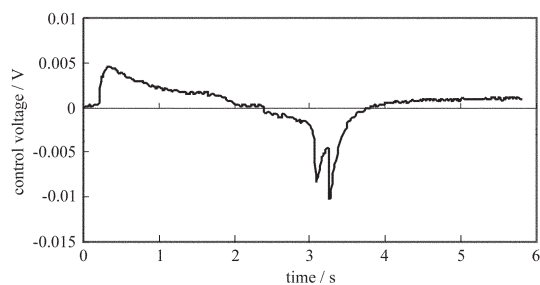


Fig.2 Control voltage trace of MnCP under 0.1 MPa Ar, the set temperature of 388 °C and the sample temperature of 368 °C

Figs.5~7 show the concentration-time profiles of the gas products quantified by T-jump/FTIR spectroscopy for MnCP, NiCP and PbCP under 0.1MPa Ar and the corresponding temperature. The temperatures

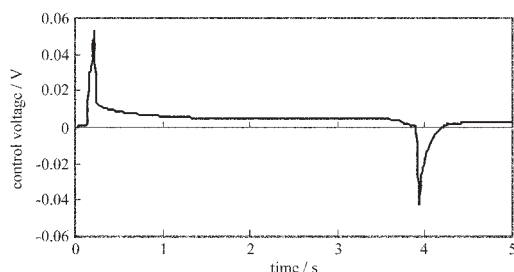


Fig.3 Control voltage trace of NiCP under 0.1MPa Ar, the set temperature of 368 °C and the sample temperature of 345 °C

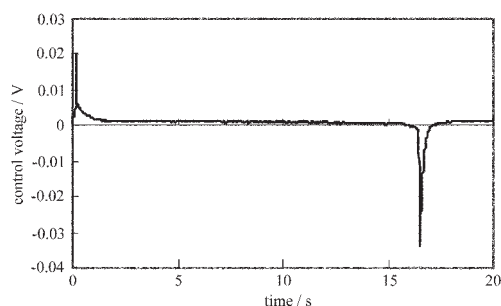


Fig.4 Control voltage trace of PbCP under 0.1MPa Ar, the set temperature of 365 °C and the sample temperature of 348 °C

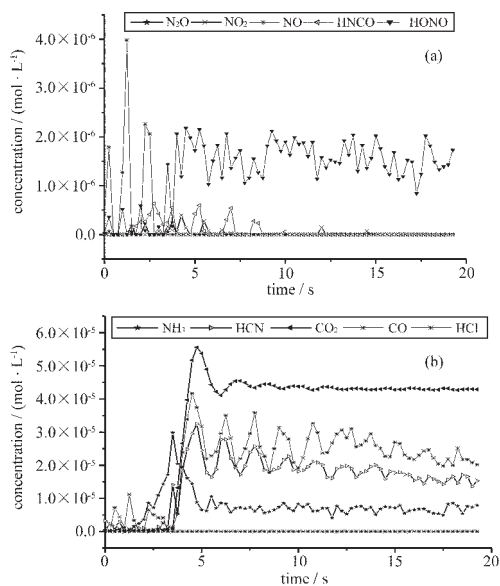


Fig.5 Concentration-time profiles of the gas products (excluding H_2O and $\text{H}_2\text{C}=\text{O}$) from MnCP at 0.1 MPa Ar

shown are 388 °C (MnCP), 368 °C (NiCP) and 365 °C (PbCP) and are 50~90 °C above the decomposition temperatures by differential scanning calorimetry(DSC) and TGA methods. Excluded from these plots are H_2O

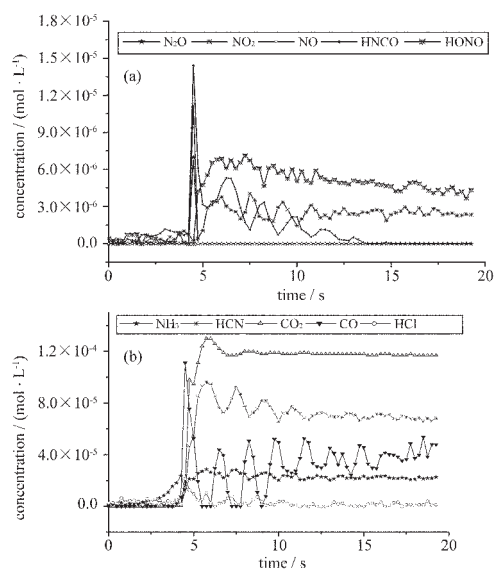


Fig.6 Concentration-time profiles of the gas products (excluding H_2O and $\text{H}_2\text{C}=\text{O}$) from NiCP at 0.1 MPa Ar

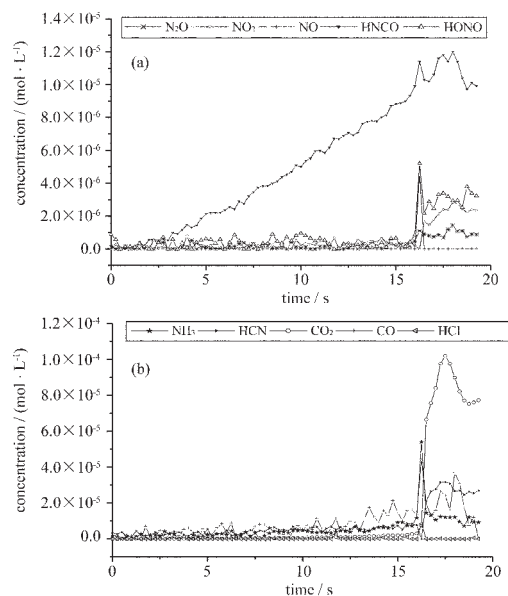


Fig.7 Concentration-time profiles of the gas products (excluding H_2O and $\text{H}_2\text{C}=\text{O}$) from PbCP at 0.1 MPa Ar

and a small amount of $\text{H}_2\text{C}=\text{O}$. H_2O was detected in the gas products in high concentration but was not quantified. As shown in Fig.5, the IR active gas products first detected consisted of N_2O , NO , NH_3 , CO and HNCO . Accompanied by the formation of the five gas products, there existed an endothermic process. The formation of NO_2 , HCN , HCl , HONO and CO_2 followed with the endothermic process. From Fig.5, we know that the process of MnCP sends out heat sharply. Fig.

6 shows the main gas products of NiCP at 0.1 MPa Ar. Dissimilar to MnCP, NH_3 and NO_2 are the gas products first detected, quickly followed by other eight gas products. While the IR active gas products during PbCP's decomposition initially detected consisted of NO, HCl and HNCO (shown in Fig.7) and the other seven products evolved along with the exothermic process later.

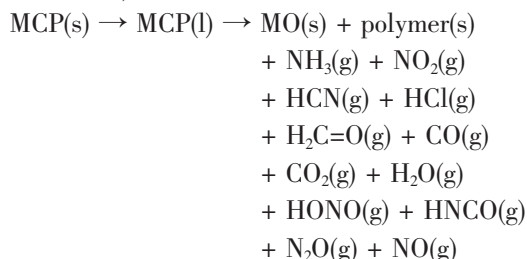
From comparing Figs.5~7, it is apparent that some resemblances exist in the decomposition characteristics of MnCP, NiCP and PbCP. For example, twelve gas products are resolved during the flash pyrolysis process, of which CO_2 is the dominant decomposition product of the residue under 0.1 MPa Ar; a large amount of HCN indicates a high percentage of azine linkages in the residue^[13]; there exists gaseous NO_2 in the products, which indicates that some of the $-\text{NO}_2$ functional groups are retained by the residue up to the set temperature. The concentration of NH_3 and HCl spikes to the maximum then decreases gradually. This is because NH_4Cl can be produced in the duration of the experiment; NH_4Cl then decomposes into NH_3 and HCl further at high temperatures, NH_3 is oxidized to NO_2 , N_2O and H_2O as the decomposition rapidly accelerates. At least some of the N_2O may result from this reaction. In addition, it should be noted that the concentration of the products varies somewhat, which may be attributed to the effects of air bubbles. It is possible that the decomposition of these compounds is so abrupt that a number of air bubbles can be produced.

There are also many differences in the decomposition processes of MnCP, NiCP and PbCP, but the correlation between the center metals and the differences is not clear. Possibly the effects of the different center metal compete in a complex manner. HCN and HONO are the dominant N-containing gases for MnCP. There is only a small amount of other N-containing gases such as NO, HNCO, NO_2 and N_2O , while HCN and HNCO are the most novel N-containing gases for NiCP and PbCP, the concentrations of HONO, NO_2 and N_2O for NiCP and PbCP are much higher than those of MnCP. Generally HCN is the dominant N-containing gas for the three complexes and the concentration-time change curve of PbCP is quite different from the other two complexes.

Increasing the temperature causes NO and CO to decrease and HNCO to increase from MnCP; while the

concentration of NO, CO and HNCO from NiCP increases as the temperature increases; correlations between the concentration of the decomposition products and the temperature are not clear for PbCP, in general, increasing the temperature has little effect on the concentration of NO, CO and HNCO.

As mentioned above, the decomposition processes of the three complexes consist of one endothermic process and one intense exothermic process (or two successive exothermic processes); their flash pyrolysis mechanisms are characteristic of dynamites and explosives. The flash pyrolysis mechanism of the three complexes can be expressed by the following scheme^[9] (M=Mn, Ni, Pb):



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