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## Study on Rapid Thermolysis of $[Cd(CHZ)_3](ClO_4)_2$

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**Abstract:** To investigate the thermal decomposition behavior of  $[Cd(CHZ)_3](ClO_4)_2$  (CdCP), the T-jump/FT-IR spectroscopy was used to determine the main gaseous products evolved from the thermolysis of CdCP in real time. CdCP was flash-pyrolyzed at  $200\text{ }^\circ\text{C} \cdot \text{s}^{-1}$  to the set temperature under different pressures. With the help of rapid scanning Fourier transform infrared FT-IR spectroscopy, 11 IR-active gas products were resolved during the flash pyrolysis process. The change curves of the concentration of the main gaseous products *vs.* time were given, indicating that over the range of pressure from 1.0 to 15 atm, the thermal decomposition behavior of CdCP does not seem to be obviously affected by the pressure.

**Key words:** analytical chemistry; cadmium perchlorate; carbonylhydrazide; rapid thermolysis; T-jump/FT-IR

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### 1 Introduction

$[Cd(CHZ)_3](ClO_4)_2$  (CdCP) can be synthesized according to the reported method<sup>[1]</sup>. It is a gemlike white crystal and it is indissoluble in many organic solvents such as alcohol, ether, halide and so on. It can be used as new kind of insensitive primary explosive, what's more, it shows good fluidity and it is convenient for loading application. Meanwhile, its friction, impact and flame sensitivities are lower than the usual propellants. All these properties are highly desirable for the security of the propellants. It has already been used as explosive to bring in satisfactory social benefit and economical benefit in industry. In order to research and develop new insensitive powerful primary explosives, a series of coordination compounds were made of carbonylhydrazide as ligand with heavy metal ions in the past few years<sup>[2,3]</sup>, their thermal decomposition mechanisms of these organic compounds were studied by using DSC, TG-DTG and FT-IR technology.

It is widely accepted that significant chemistry can

occur in the surface layer. Determination of the reactions is experimentally very difficult because the surface layer is thin and transient during combustion. However, an instantaneous simulation of the burning surface can be obtained by rapidly heating a thin film of material to the burning surface temperature. In this paper, we studied the evolved gas products of CdCP during the flash pyrolysis process and put forward the concentration change curve of the main gaseous products.

### 2 Experimental

#### 2.1 Sample and experimental apparatus

Sample of  $[Cd(CHZ)_3](ClO_4)_2$  (CdCP) was self-synthesized according to the previous method<sup>[4]</sup>, further purification was also attempted in several instances. A Nicolet 20 SXB FTIR spectrometer with an MCT detector was used to record the IR spectra as the sample heated. The rapid thermal decomposition of CdCP was examined by rapid-scan FTIR spectroscopy<sup>[5,6]</sup>.

The experimental data was collected from the PC computer and the data processing was accomplished by using the Matlab procedure, thus we can get the gas products during the flash pyrolysis process and put forward the concentration change curve of the main gaseous remains simultaneously.

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## 2.2 T-Jump / FTIR spectroscopy

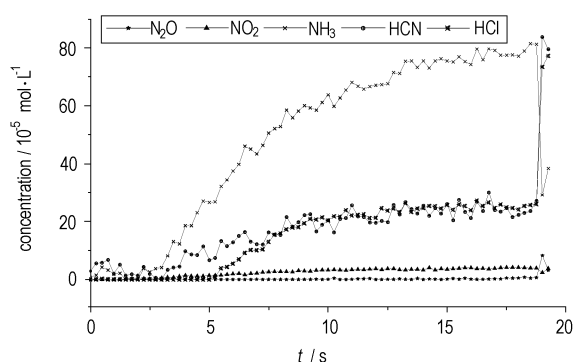
A sample of approximately 0.5 mg of CdCP was thinly spread on the center of the Pt filament and inserted into the spectroscopy cell<sup>[5]</sup>. After purging the cell with 1 atm Ar, the filament was heated to the set temperature. The high-gain, fast-response, power circuit<sup>[5]</sup> that controls the temperature of the Pt filament is sufficiently sensitive that the control voltage can detect thermal events occurring within the sample as it decomposes. To maintain the filament at a constant temperature (resistance), the circuit adds current when the sample is undergoing an endothermic event. Similarly, the current is reduced when an exothermic event occurs. When the control voltage trace of the filament with no sample present is subtracted from the trace of the filament at the same conditions with the sample in place, these endothermic and exothermic events are evident as positive and negative inflections, respectively.

IR spectra of the evolved gaseous products were recorded with  $4\text{ cm}^{-1}$  resolution with an FTIR spectrometer (Nicolet 800). The cell contained Ar at 1 atm and was initially at room temperature. Thus, the reaction products were thermally quenched before they reached the IR beam.

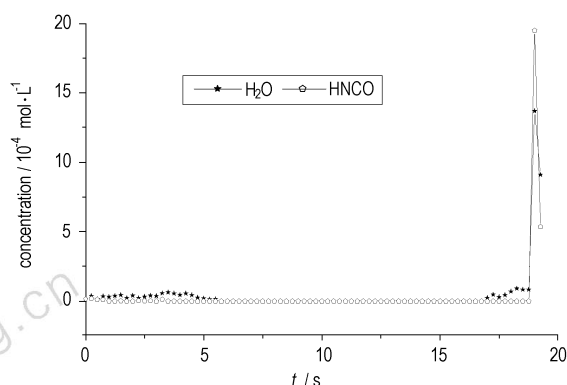
## 3 Results and discussion

Figure 1 shows the change of concentration of the main gas products from CdCP measured by rapid-scan FTIR spectroscopy at 1 atm Ar. As there only exists a small amount of CO and HONO, these two gas products are excluded from these plots. As shown in Fig. 1, the dominant gas product of the evolved gas products is  $\text{NH}_3$ , The IR active gas products are first detected at about 2 s and consist of  $\text{NO}_2$ ,  $\text{NH}_3$  and HCN. The formation of HCl and  $\text{H}_2\text{C}=\text{O}$  ensues. A rise in the concentration of all these five gas products indicates that the amount of sample decomposing gradually increases. The overall process is endothermic because the inflection of the control voltage is positive during this time (as shown in Fig. 2). Under the conditions of this experiment,  $\text{NH}_3$  and HCl arise from the pyrolysis species:  $\text{NH}_4\text{Cl}$ . It is commonly believed that reaction (1) is endothermic. Additionally, the heat formation of HCN is positive, so accompanied by the formation of these products, there exists an endothermic process. HNCO,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2\text{O}$  are detected near

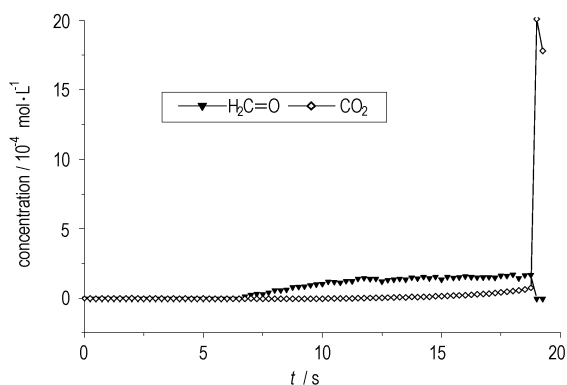
the end of the decomposition process (at about 18 s), besides their concentrations rise abruptly to the maximum, we can make certain that the decomposition process sends out heat sharply from the intense negative inflection in the control voltage at this time (as shown in Fig. 2). The exothermic process is caused by the intense secondary intermolecular reactions<sup>[7]</sup>, above all things is the oxidation-reduction reaction between  $\text{NH}_3$  and  $\text{NO}_2$ , at higher temperature some of the  $\text{NH}_3$  is oxidized in the following reaction (2).



(a)



(b)



(c)

Fig. 1 The IR active gas products evolved from the thermolysis of CdCP at 1 atm Ar

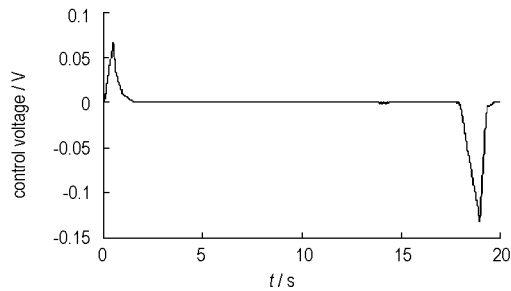
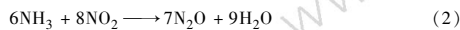
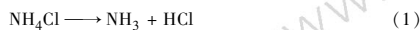


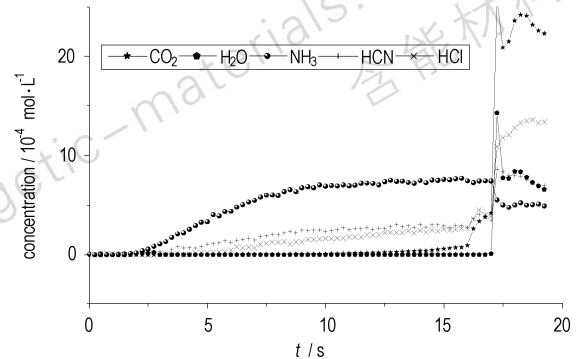
Fig. 2 The control voltage trace of CdCP



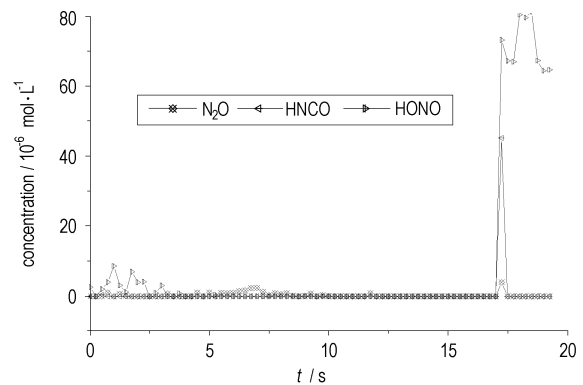
As shown in Fig. 3,  $\text{NH}_3$  is also the dominant decomposition product of the evolved gas products under 15 atm Ar. Likewise, the IR active gas products detected initially consist of  $\text{NO}_2$ ,  $\text{NH}_3$  and  $\text{HCN}$ , quickly followed by  $\text{HCl}$  and  $\text{H}_2\text{C}=\text{O}$ . Compared with Fig. 2, the concentration change trends of  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{H}_2\text{C}=\text{O}$  and  $\text{HCN}$  are found to be quite similar and the concentrations of these products are not changed markedly (shown in Table 1). The formation of  $\text{HNCO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is also near the end of the decomposition, which is consistent with the former. Consequently, the concentration of these products is much less pressure dependent and the overall decomposition mechanism appears to be similar in this pressure range.

It should be noted that the concentration of the products oscillates, which may be attributed to the effects of air bubbles. It is possible that the decomposition of CdCP is so abrupt that a number of air bubbles produce. The concentrations of  $\text{NH}_3$  and  $\text{HCl}$  increase gradually, that's because  $\text{NH}_4\text{Cl}$  can be produced for the duration of the experiment,  $\text{NH}_4\text{Cl}$  then breaks up into  $\text{NH}_3$  and  $\text{HCl}$  further under the high temperature circumstance.  $\text{HNCO}$  can be produced by decomposition of the amide unit (I) [7,8] and  $\text{HCN}$  can form from polyazine unit (II) [9]. The high concentration of  $\text{HCN}$  along with the IR spectrum of the products indicates a high percentage of azine linkages in the gas products [10]. The sustained presence of gaseous  $\text{NO}_2$  indicates that some of the  $-\text{NO}_2$  functional groups are retained by the products up to 368 °C. In addition, there exists no nitrogen monoxide in the evolved gas products. In sum, we can infer that the gas products are relatively stable. Not surprisingly, the concentrations of these

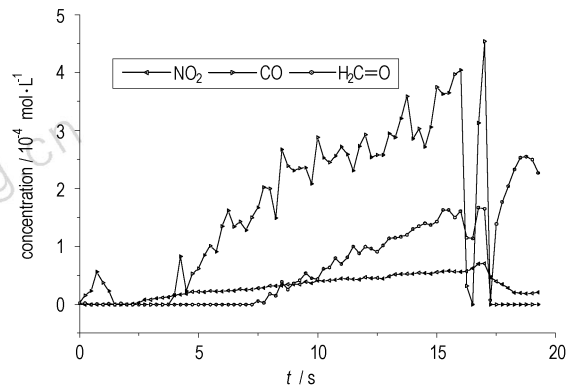
products are less dependent on the applied pressure (at relatively low pressure).



(a)



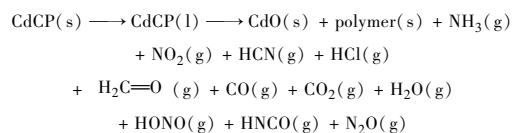
(b)



(c)

Fig. 3 The IR active gas products evolved from the thermolysis of CdCP at 15 atm Ar

As mentioned above, the mechanism of the high-rate thermal decomposition of CdCP can be expressed by the following scheme [11]:



**Table 1 The maximum concentration of the followed gas products at different pressures**

gas products	maximum concentration/ $10^{-5} \text{ mol} \cdot \text{L}^{-1}$	
	at 1 atm Ar	at 15 atm Ar
HCl	10.0	14.0
HCN	8.4	9.0
$\text{NH}_3$	8.0	7.8
$\text{H}_2\text{C}=\text{O}$	1.9	2.5
$\text{NO}_2$	0.4	0.7

## 4 Conclusions

(1) The decomposition process of CdCP consists of one endothermic process and one intense exothermic process, its high-rate thermal decomposition mechanism is characteristic of dynamites and explosives.

(2) CdCP decomposes abruptly, which leads to the oscillation of concentration of the gas products detected. Because CdCP melts initially, then decomposes, the gas products evolve at different time, thus the concentrations of the products change with time.

(3) 11 specific products ( $\text{NO}_2$ ,  $\text{NH}_4\text{Cl}$  (broken up into  $\text{NH}_3$  and HCl later) HCN,  $\text{H}_2\text{C}=\text{O}$ , CO and so on) are resolved as a function of concentration and time, of which  $\text{NH}_3$  is the most novel IR active product,  $\text{NH}_3$ ,  $\text{NO}_2$  and HCN are the dominant gases containing nitrogen and there also exists a spot of HNCO, HONO and  $\text{N}_2\text{O}$ , the dominant gases containing carbon are  $\text{H}_2\text{C}=\text{O}$  and CO and there exists traces of  $\text{CO}_2$  additionally.

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## [ Cd(CHZ)<sub>3</sub> ](ClO<sub>4</sub>)<sub>2</sub> 的快速热分解过程研究

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**摘要:** 为了考察[ Cd(CHZ)<sub>3</sub> ](ClO<sub>4</sub>)<sub>2</sub> (CdCP)的热分解行为,采用 T-jump/FT-IR 光谱法实时测定了 CdCP 的快速热分解气体产物。CdCP 在不同的压力下以 200 °C · s<sup>-1</sup> 的升温速率达到设定的温度快速分解。用快速扫描傅立叶变换红外光谱,解析了解过程中逸出的 11 种红外活性气体,给出了主要气相产物浓度随时间的变化曲线。结果表明,在 1.0 ~ 15 atm 范围内,压力不影响 CdCP 的热分解行为。

**关键词:** 分析化学; 高氯酸镉; 碳酰肼; 快速热分解; T-jump/FT-IR

**中图分类号:** TQ564.4

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