

Thermal Decomposition of CS by TG/DSC-FITR and PY-GC/MS

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Abstract — As an excellent tear agent of the second generation, CS has been widely used in the police department of many countries. CS disperses the crowd depending on the aerosol in the air due to combustion and explosion. And at the same time, CS decomposes into a variety of products. With the use of TG/DSC-FITR and PY-GC/MS technologies, the CS decomposition performance has been studied. It has been found that CS begins to melt at 60°C, boiling near 310°C and decompose between 450°C to 550°C. There is a close relationship between thermal decomposition products and the temperature. At 550°C and 650°C, 4 and 10 kinds of decomposition products will be produced respectively.

Keywords-2-Chlorobenzalmalononitrile; thermal analysis; FITR; PY; gas chromatography (GC); mass spectrometry (MS); thermal decomposition

I. INTRODUCTION

2-Chlorobenzalmalononitrile was firstly synthesized by Corson.B.S and Stroughton.R.W in the United States in 1928 [1]. The first letter of the two surnames were taken to name CS. CS has strong stimulation to the eyes, skin and upper respiratory tract and can cause temporary incapacitating [2, 3]. In 1950s, the CS stimulation effect is 10 times stronger than chloroacetophenon (CN) and does less damage to the human body than diphenylcyanoarsine and diphenylchloroarsine after the test [4]. In 1959, CS acting as the second generation of riot control agent with the excellent performance was equipped with US and as the irritant used many times during the Vietnam War with the amount of 7000 tons and then obtained the widespread application in the police department of many countries [5].

In the application, CS makes up a mixture with combustion agent or explosive composition. CS dispersed in air to form aerosol through thermal or explosion effects and it will have effect on the dispersion of the crowd [6]. The high-temperature will be produced in pyrotechnic combustion and explosion process and the CS will be decomposed at the same time. The study of the thermal decomposition of CS at different temperature and

determining the decomposition products under corresponding temperature have practical significance. One thing is to provide the theoretical basis for the explosive formulation, that is, the ammunition power will be improved due to the reduction of decomposition of CS by adjusting the temperature of combustion and explosion. The second thing is to determine the decomposition products and understand its toxicity to human body, so as to provide reference opinion on how to use the CS. The third thing is to select a suitable temperature when using the incineration destruction of abandoned CS riot ammunition to Control the incineration products and reduce the pollution of the environment. Wang Xuan-yu [7] did the research of the effects of different temperature on incineration destruction of CS through experiment.

Literature [8] studied the probability of generating HNC and HCL in CS thermal decomposition at high temperature (more than 700°C). Literature [9] used Teflon filters to collect CS thermal decomposition products and analyses the composition of products by GC-MS technology, but did not specify the temperature of thermal decomposition. The combination of hot furnace and temperament pipe technology has been used in research of CS decomposition product at 300-900°C in the literature [10]. Literature [11] used solid phase microextraction and GC-MS technology to collect and analysis the CS decomposition product at 150-300°C and the relationship between the product and the temperature of decomposition has been studied. In the above researches, the CS heating rate is low. The thermal decomposition of CS is actually lower than the set temperature value following a series of temperatures, which are gradually decomposed and occurred in a variety of reaction process. Besides, some thermal decomposition products did not come into the chromatographic analysis quickly, namely the existence of secondary reaction problems.

In the paper, TG/DSC-FITR and PY-GC/MS techniques have been used to do CS thermal decomposition research. Combined with DSC, the solid state CS weightlessness when heating and the

corresponding thermal effects can be studied. FTIR can identify the evolved gases qualitatively. In PY-GC/MS study, thermal cracking device can be warmed rapidly at a rate of about 3000°C/s, and the sample fall into the cracker freely when it reaches to the set temperature. The experimental samples are µg level. The dead volume in the cracking reactor is very small and concentration of pyrolysis products is very low. The above aspects can ensure the CS thermal decomposition in precise temperature and decrease secondary reaction and can simulate the CS explosion thermal process well.

II. EXPERIMENTAL

A. Experimental Materials

2-Chlorobenzalmalononitrile, with formula is C₁₀H₅ClN₂, CAS No: 2698-41-1, light yellow powder, was purchased from Hubei Southern Star Chemical Plant, purity: HPLC98%. Fig .1 is the structure of Matter With Gaussian03 software optimization.

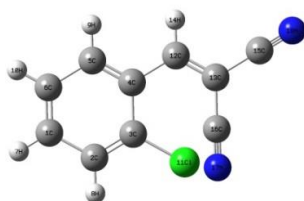


Figure 1. The structure of CS

B. Apparatus of Experiment

1) TG/DSC-FTIR

Simultaneous thermal analysis: Germany Netasch company 449F3 type TG/DSC simultaneous thermal analyzer. Temperature Range: -120-2400 °C ; mass resolution: 0.1µg; heat sensitivity: <1µW; heating rate: 0.001-50 °C /min; vacuum degree: 10-4mbar; infrared connection port temperature: room temperature - 300°C.

Infrared Spectrometer: German Bruker VERTEX 70v type; Beamsplitter: KBr-on-Ge; Detector: MCT type; spectral range: 25,000-20 cm⁻¹; spectral resolution: 0.4cm⁻¹; fast scan rate:80file/s (16cm⁻¹ resolution); wavenumber precision: 0.01 cm⁻¹, In situ gas cell temperature: room temperature-230 °C ; MS transfer line temperature: room temperature-230°C.

2) PY-GC/MS

Gas chromatography-mass spectrometry:Shimadzu of Japan, GCMS-QP2010SE type, tube furnace cracker: Japan Frontier, EGA / PY-3030D Type.

C. Test conditions

1) TG/DSC-FTIR

Thermal Analyzer crucible type: aluminum pool; carrier gas: air; purge gas flow rate: 50ml / min; protective gas flow: 25ml/min; temperature range: 50-550°C, heating rate of 5 °C /min, the sample mass 5mg. Selected wavenumber range: 4000-650 cm⁻¹; infrared gas tank and combined with transmission line temperature were 200°C.

2) PY-GC/MS

Cracker conditions: pyrolysis temperature 350-650°C, increments to 100°C; pyrolysis time was 30s; the air was

filled with Cracking Furnace, argon as the carrier gas. Chromatographic conditions: inlet temperature is 280°C; sample Initial temperature was 50°C,keep one minute, by 8°C/min rate rose to 300°C; Capillary Column: Agilent company Ultra alloy-5 type, specifications: 30m×0.25mm ×0.25µm; argon as the carrier gas. MS conditions: ion source: EI; voltage: 70eV; scan range: amu 33-600; detector temperature: 250°C.

III. RESULTS AND ANALYSIS

A. Results of TG and DSC

Fig .2 tells that the change of heat and calorimetry of CS when the decomposition temperature rise from 25°C degree to 600°C degree at the heating rate of 5°C degree per minute.

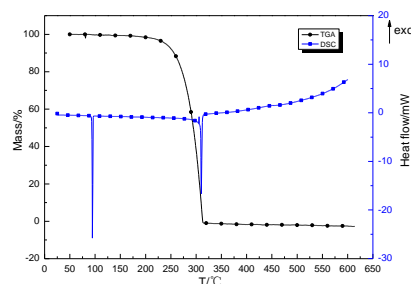


Figure 2. The curves of TGA and DSC of CS

It's obviously that the substance was being lost weight since from the temperature close to 270°C degree and the rate of lose rose to top when the temperature close to 310°C degree. So it's proved that CS has been evaporated or decomposed during the time. On the other hand there are two endothermic peaks whose temperature were at 90°C degree to 100°C degree and 300°C degree to 310°C degree, where the quality of the former called melting peak was unchanged and another was rapidly decreased.

B. Results of FTIR

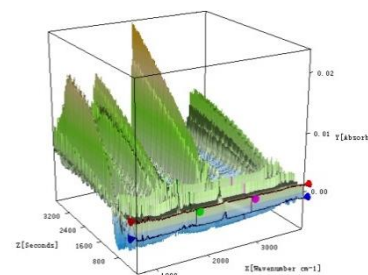


Figure 3. The three-dimensional infrared spectral of gas products of CS during heating decomposition

Fig .3 is a gas generating three-dimensional infrared spectra of CS at a heating rate of 5°C/min rise from 25°C to 320°C. In the heating process, spectral absorption peak position did not change, just as the temperature rises, the gasification of CS increase and absorbance increases of Corresponding groups. When the temperature at 310 °C degree (3400s) or so, the absorbance maximum of each

group, combined TGA/DSC curves and spectra analysis, CS decomposition did not happen at this time, should be boiling peak. Integrated with knowledge, When CS in a 5°C/min heating rate of

heating, gasification melting and boiling occurs first, no decomposition occurs before boiling.

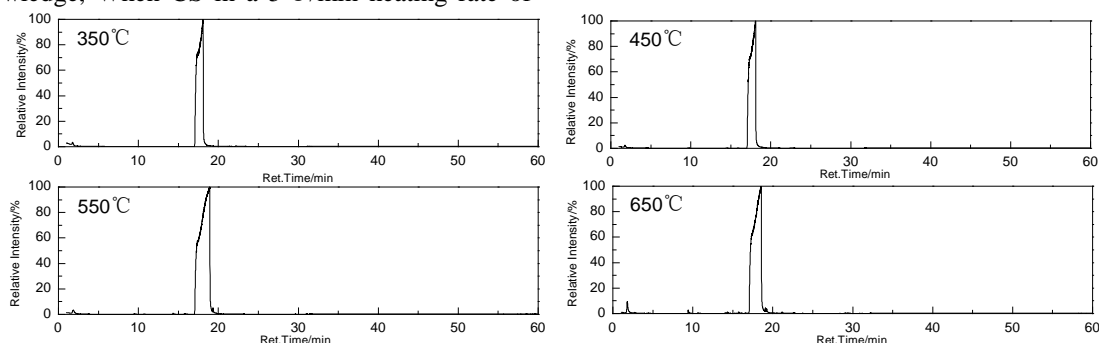


Figure 4. The ion flow of cracking products of CS at 350°C、450°C、550°C and 650°C

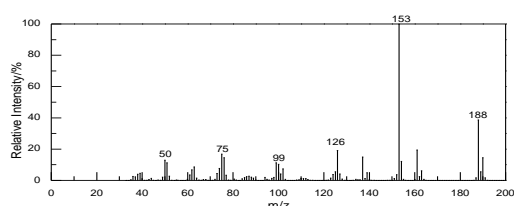


Figure 5. The mass spectrum of CS

C. Results of PY-GC/MS

In the experiment, first of all, heat the pyrolyzer to specified temperature and then put sample in it by falling free, which is guaranteed that the sample is being cracking on the specified temperature which has been set up. When it close to the specified time has been set up, the cracking

products were brought into the gas chromatograph by argon and separated, then the products would be entered into the system of mass spectral analysis. (Fig .4)

What the first two of the Fig .4 show is that there was only one small peak except the base peak when the retention time was nineteen minute and it proved that the peak represent for argon after mass spectral analysis. So it's apparent that the CS haven't broken down at 350°C degree and 450°C degree, but when the temperature rise to 550°C degree, then the gas chromatograms show many peak which is mean CS has been broken down and had initial cracking products.(Fig .6)

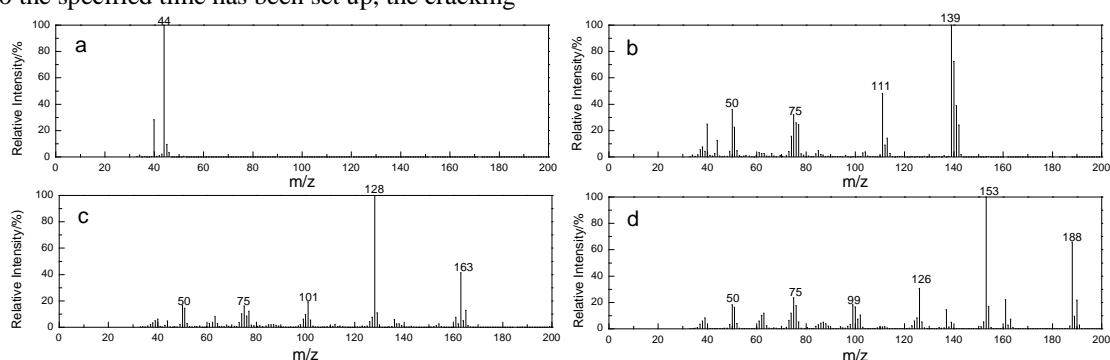


Figure 6. The mass spectrum of products of CS cracked at 550°C degree

Because there is CS in cracking products at each temperature point, Fig .5 is the mass spectrum of CS. What the Fig .6 and Fig .7 tell is the mass spectral analysis of cracking products of CS at 550°C and 650°C degree . Table.1 is cracking products of each temperature which is based on the spectral through searching and artificial analyzing. What we got from the chromatogram was that there was five cracking products at 550°C degree and ten at 650°C degree. On the other hand, two more isomers has been found from the cracking products, which was called for Benzene,1-Chloro-4-(2,2-dicyanoethenyl and Benzene,1-Chloro-3-(2,2-dicyanoethenyl. The

retention time was much closed between those products and CS on the chromatogram, it presented that the proportion of mass and electric charge was close, but what the difference was the value of abundance. Besides, another product which was called 1,1':2',1''-Terphenyl, 2,5-dichloro- was found in the cracking products when the temperature was set 650 °C , why the products generated was the cracking products had already finished the secondary reaction under the exactly temperature. Furthermore, the relative molecular weight of it was heavier than CS.

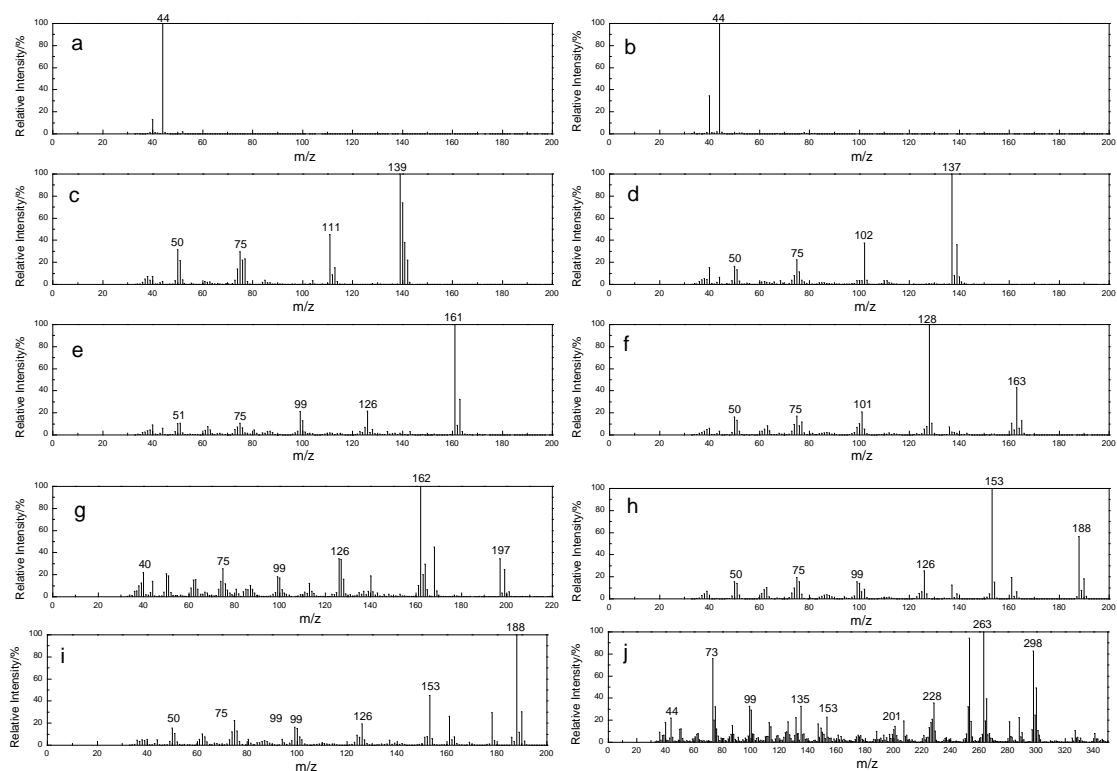


Figure 7. The mass spectrum of products of CS cracked at 650°C degree

TABLE I. THE CRACKING PRODUCTS OF CS AT THE TEMPERATURE OF 350°C、450°C、550°C AND 650°C

| Temp/°C | No | Compound | Structural formula | retention time/min |
|---------|----|--|--------------------|--------------------|
| 350 | a | 2-Chlorobenzalmalononitrile | $C_{10}H_5ClN_2$ | 17.76 |
| 450 | a | 2-Chlorobenzalmalononitrile | $C_{10}H_5ClN_2$ | 17.735 |
| 550 | a | l-Alanine ethylamide, (S)- | $C_5H_{12}N_2O$ | 1.875 |
| | b | Benzaldehyde, 2-chloro- | C_7H_5ClO | 9.45 |
| | c | Quinoline, 2-chloro | C_9H_6ClN | 14.33 |
| | d | Benzene, 1-chloro-4-(2,2-dicyanoethenyl) | $C_{10}H_5ClN_2$ | 18.52 |
| 650 | | 2-Chlorobenzalmalononitrile | $C_{10}H_5ClN_2$ | 19.335 |
| | a | 1,2-Propanediamine | $C_3H_{10}N_2$ | 1.850 |
| | b | l-Alanine ethylamide, (S)- | $C_5H_{12}N_2O$ | 2.715 |
| | c | Benzaldehyde, 2-chloro- | C_7H_5ClO | 9.425 |
| | d | benzonitrile, 2-chloro- | C_7H_4ClN | 10.6 |
| | e | Benzenamine, 2,5-dichloro- | $C_6H_5Cl_2N$ | 14.03 |
| | f | Quinoline, 2-chloro- | C_9H_6ClN | 14.34 |
| | g | Quinoline, 2,4-dichloro | $C_9H_5Cl_2N$ | 15.385 |
| | | 2-Chlorobenzalmalononitrile | $C_{10}H_5ClN_2$ | 18.035 |
| | h | Benzene, 1-Chloro-4-(2,2-dicyanoethenyl) | $C_{10}H_5ClN_2$ | 19.065 |
| | i | Benzene, 1-Chloro-3-(2,2-dicyanoethenyl) | $C_{10}H_5ClN_2$ | 21.145 |
| | j | 1,1':2',1''-Terphenyl, 2,5-dichloro- | $C_{18}H_{12}Cl_2$ | 29.115 |

IV. CONCLUSIONS AND DISCUSSIONS

There are three conclusions about the thermal cracking of CS:

First, the melting point of CS is in the vicinity of 60°C and the boiling point near to 310°C. At the same time, the CS would not decompose heating at the rate of 5°C degree per minute before it boiled.

Secondly, the temperature of first heat decomposition was between 400°C degree and 500°C degree.

Thirdly, there are four products which CS was decomposed at 550°C degree, but the 650°C degree got more. At the same time, the cracking products have conduct the secondary reaction on the condition of the time of heat decomposition was thirty seconds.

REFERENCES

- [1] Corson B B, Stoughton R W. Reactions of alpha,beta-unsaturated dinitriles[J]. Journal of American Chemical Society, 1928, 50(10): 2825-2837. Corson, B. B.
- [2] Olajos E J, Salem H. Riot control agents: pharmacology, toxicology, biochemistry and chemistry[J]. Journal of Applied Toxicology, 2001, 21(5): 355-391.
- [3] Blain P G. Tear gases and irritant incapacitants[J]. Toxicological reviews, 2003, 22(2): 103-110.
- [4] ZHAO Shan-dong, MA Yong-zhong. Non-lethal Weapons and Police equipment [M]. Beijing: arms industry Press, 2005: 16-18.
- [5] CHEN Ji-sheng. Chemical & Biological Weapons and Equipment for Chemical Defence [M]. Beijing: Atomic Energy Press, 2003: 33-34.
- [6] ZHAO Guo-hui, CHEN Hai-ping, DONG Han-chang. Chemical Weapons [M]. Beijing: arms industry Press, 1991: 218-220.
- [7] WANG Xuan-yu, WANG Li-na. Principle and Optimized Parameters for Destroying CS by an Incinerator, Chinese [J]. Journal of Energetic Materials, 2013, 21(1): 103-107.
- [8] Kluchinsky T A, Savage P B, Fitz R, et al. Liberation of hydrogen cyanide and hydrogen chloride during high-temperature dispersion of CS riot control agent [J]. AIHA Journal, 2002, 63(4): 493-496.
- [9] Kluchinsky T A, Savage P B, Sheely M V, et al. Identification of CS-derived compounds formed during heat-dispersion of CS riot control agent [J]. Journal of Microcolumn Separations, 2001, 13(5): 186-190.
- [10] Kluchinsky Jr T A, Sheely M V, Savage P B, et al. Formation of 2-chlorobenzylidenemalononitrile (CS riot control agent) thermal degradation products at elevated temperatures [J]. Journal of Chromatography A, 2002, 952(1): 205-213.
- [11] Hook G L, LaPuma P T, et al. Identification of Compounds Formed During Low Temperature Thermal Dispersion of Encapsulated o-Chlorobenzylidene Malononitrile (CS Riot Control Agent) [J]. Journal of occupational and environmental hygiene, 2010, 7(6): 352-357.