

Synthesis of unsymmetrical dimethylhydrazine oxalate from rejected liquid rocket propellant

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Abstract: The rejected liquid propellant unsymmetrical dimethylhydrazine (UDMH) was converted to UDMH oxalate, which has commercial value. The UDMH oxalate structure and stability were investigated by the Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and ultraviolet-visible spectrophotometric analysis. The results indicate that UDMH oxalate has good thermal and aqueous solution stability, a melting point of 144 °C, an initial decomposition temperature of 180 °C, and a peak wavelength of UV in aqueous solution at $\lambda = 204$ nm. This disposal method of rejected UDMH is highly efficient and environmentally safe.

1. Introduction

Large quantities of unsymmetrical dimethylhydrazine (UDMH) have been produced worldwide for their use as a liquid rocket propellant. However, UDMH is inflammable, explosive, volatile, mutagenic, and a suspected carcinogenic compound [1-3], posing a serious threat to ecological environment and human health. Every year, a large amount of rejected UDMH is generated due to long-term storage, routine maintenance, laboratory sampling, and other factors. Great amounts of manpower, material and financial resources have been consumed to dispose the waste.

Catalytic oxidation has been used in the disposal of rejected UDMH [4-6], where the UDMH is decomposed and produces many harmless small molecules. The reaction of UDMH decomposition is usually incomplete, and some of the products formed are even more harmful than UDMH [7-8]. Researchers in the US and Russia have conducted much research [9-13] on the technology of reusing rejected UDMH, but most of these studies are still in the stage of laboratory study. Hence, it is urgent to develop a new way of disposing rejected UDMH efficiently and environmentally safely.

In this paper, UDMH is converted to UDMH oxalate, which is a new high-added value product widely used in the synthesis of Gemini surfactant and nuclear fuel reprocessing Purex process [14-15]. The solid UDMH oxalate is easily produced when UDMH reacts with a saturated solution of oxalic acid in absolute ethanol. Compared with liquid UDMH, UDMH oxalate has excellent stability, making its storage safe and easy. If needed, it can also produce liquid UDMH reversely. This method seems very promising in the disposal of rejected UDMH.

2. Experimental

2.1. Theoretical background

Based on the theory of acid-base reaction, the weak base UDMH should readily react with the weak acid oxalic acid and abide by the following reaction:





2.2. Materials and apparatus

The new compound synthesis was conducted using rejected UDMH and oxalic acid as reaction reagents and ethanol absolute as solvent. Its structure identification was accomplished using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (1HNMR), and differential scanning calorimetry (DSC) analytical techniques. An EQUINOX55 FTIR spectrometer was used to conduct IR analysis. Its sample cell was KBr crystal. A superconducting NMR spectrometer of INOVA type made by Varian Co. was used to carry out 1HNMR analysis. CDCl₃ was selected as solvent and TMC as standard substance. The operating frequency was 400 MHz. A DSC822 type made by METTLER TOLEDO Co. was used to test thermal behavior.

2.3. Synthesis

At an oxalic acid to UDMH molar ratio of 1: 2, UDMH was first put inside a closed reactor. Under constant stirring and a reaction temperature of 25 °C, crystal precipitation soon formed after the saturated oxalic acid solution of ethanol absolute was added into the reactor. White needle-like UDMH oxalate crystals were finally produced after the processes of vacuum filtration, washing with ethanol, purification, and dehydration.

3. Results and discussion

3.1. Characterization of UDMH oxalate

Figure 1 shows the IR spectrum of UDMH oxalate, whereas the peak frequencies are given in Table 1. Table 2 shows the 1HNMR data explaining Figure 2. Figure 3 presents the ultraviolet (UV) adsorption spectrum of UDMH oxalate aqueous solution with a maximum adsorption peak at a wavelength of 204 nm.

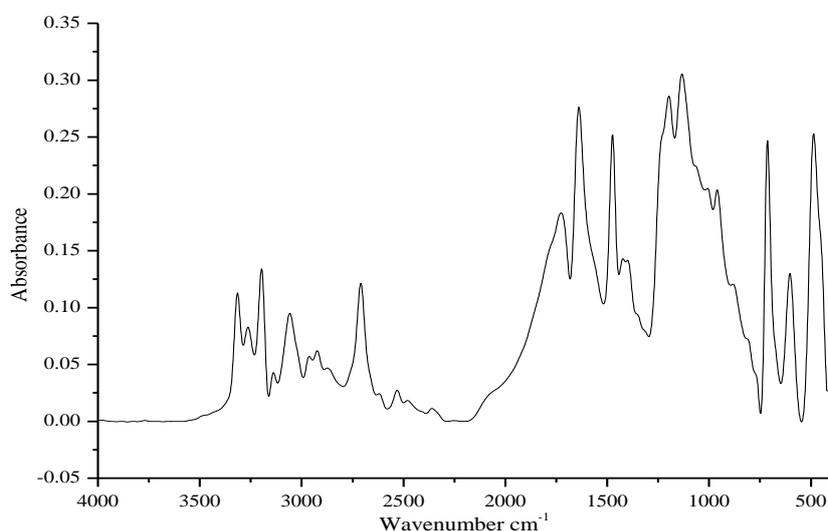


Figure 1. FTIR spectra of UDMH oxalate.

Table 1. FTIR spectra data of UDMH oxalate.

Frequency (cm ⁻¹)	Group attributed to	Vibration type
3196.66	—NH ₂	v
2709.68	—CH ₃	v
1639.27	—C=O	v
1473.99	—CH ₃	δ
947.36	O—H	δ
713.29	N—H	δ

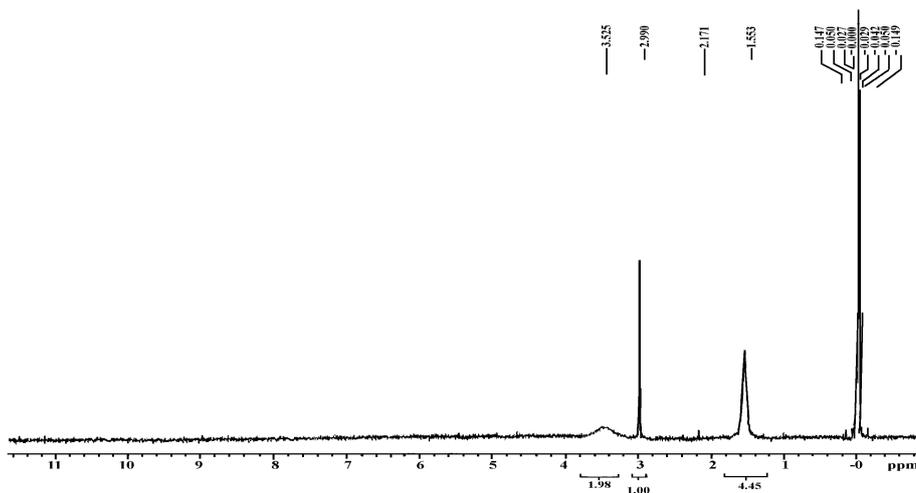


Figure 2. ¹H-NMR of UDMH oxalate.

Table 2. ¹H-NMR data of UDMH oxalate.

Chemical shift (δ /ppm)	Group attributed to
3.525	NH ₂
2.990	CH ₃
1.553	H ₂ O

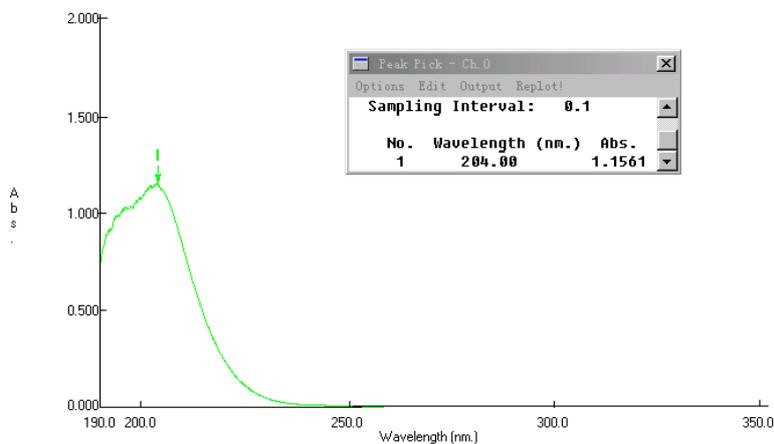


Figure 3. UV spectrum of UDMH oxalate aqueous solution (0.001mol/L).

3.2. Analysis of thermal stability

Figure 4 shows the thermogravimetric analysis plot of UDMH oxalate. Clearly, UDMH oxalate experienced two weight loss stages in the heating process. The weight loss rate of the first stage was about 9.08%, its peak temperature was 116.87°C, and the extrapolated onset temperature was about 100 °C. The first weight loss stage can be inferred as a water-loss period. The weight loss rate of the second stage was 86.11%, its peak temperature was 199.19 °C, and the extrapolated onset temperature was about 180.36°C. This finding indicates that the second weight loss stage is a decomposition period. The melting point of UDMH oxalate was tested on DSC, as shown in Figure 5. The melting point was about 144 °C.

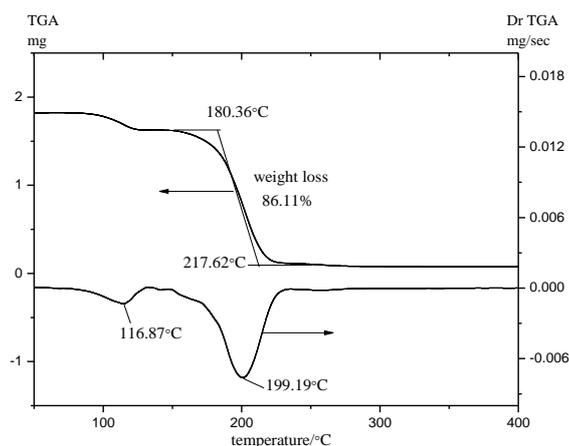


Figure 4. Thermogravimetric curve of UDMH oxalate.

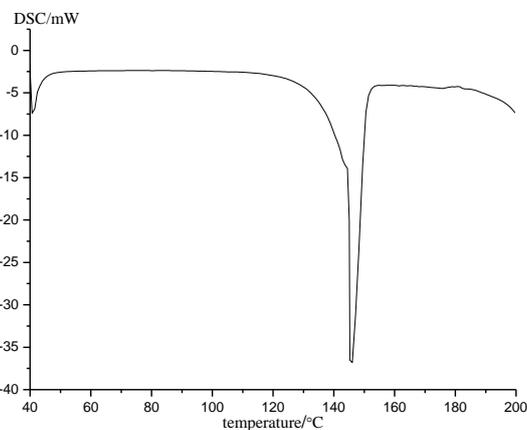


Figure 5. DSC curve of UDMH oxalate.

Based on the data above, UDMH oxalate is concluded to have good thermal stability.

3.3. Stability of UDMH oxalate in aqueous solution

A certain amount of UDMH oxalate was dissolved in water to make a saturated solution. The color change was observed and tested using the naked eye and indicator paper at a given time interval. UV spectrophotometer was also used to measure its absorbance change at $\lambda = 204$ nm (solution was diluted with distilled water with the same multiple). Results in Table 3 imply that UDMH oxalate has excellent stability in water solution at atmospheric temperature.

Table 3. Stability of UDMH oxalate aqueous solution.

Time/h	Color of solution	Color change of indicator paper	Absorbance
0	colorless	no change	2.1567
12	colorless	no change	2.1566
24	colorless	no change	2.1566
48	colorless	no change	2.1565
72	colorless	no change	2.1567

3.4. Solubility in conventional solvents

Table 4 shows the solubility of UDMH oxalate in conventional solvents. UDMH oxalate can be easily dissolved in water but difficult to be dissolved in organic solvents.

Table 4. Solubility in conventional solvents.

Solvent	Water	Ethanol absolute	Acetone	Tetrahydrofuran	Isopropanol
Solubility(g)	54.33	0.26	0.18	0.45	0.53

4. Conclusions

The conversion of UDMH oxalate from UDMH is an efficient way to solve the intractable problem of rejected UDMH treatment. This new method has been proven to be safe, efficient, and without any detrimental effects to the environment.

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