The thermal decomposition of \(N,N\)-dimethyl-3-oxa-glutaramic acid and the kinetics of its second-stage thermal decomposition reaction

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\(N,N\)-dimethyl-3-oxa-glutaramic acid was purified and characterized by \(^1\)H-NMR, Fourier transform infrared spectroscopy (FT-IR) and elemental analysis. The thermal decomposition of the title compound was studied by means of thermogravimetry differential thermogravimetry (TG-DTG) and FT-IR. The kinetic parameters of its second-stage decomposition reaction were calculated and the decomposition mechanism was discussed. The kinetic model function in a differential form, apparent activation energy and pre-exponential constant of the reaction are \(3/2 \left[1 - (1 - \alpha)^{1/3}\right] - 1\), 203.75 kJ mol\(^{-1}\) and 10\(^{17.95}\) s\(^{-1}\), respectively. The values of \(\Delta S^\ne\), \(\Delta H^\ne\) and \(\Delta G^\ne\) of the reaction are 94.28 J mol\(^{-1}\) K\(^{-1}\), 203.75 kJ mol\(^{-1}\) and 155.75 kJ mol\(^{-1}\), respectively.

1 Introduction

The treatment and disposal of the highly active wastes (HAWs) is a worldwide difficulty. The solvent extraction processes such as TRPO\(^1\) and TRUEX processes\(^2\) have been employed to remove the actinides from HAWs, for example, TRPO process, TRUEX process\(^2\). The effective stripping of actinides from the loaded extractant is a key problem. Some water-soluble oxa-amides have been found to be strong complexants for the actinides in the aqueous phase and suitable for actinides stripping from the loaded organic phase\(^3\). \(N,N\)-dime thyl-3-oxa-glutaramic acid (see Figure 1) is a typical water-soluble oxa-amide with a solubility of about 0.5 mol/L at 25°C. Compared with the phosphorus-containing compounds, \(N,N\)-dimethyl-3-oxa-glutaramic acid (DOGA) has the advantage of complete decomposition or incineration without secondary wastes because it is composed of only C, H, O, and N. It is a promising stripping agent in the treatment of HAWs.

In order to develop the decomposition technology of the spent stripping agent, the thermal decomposition mechanism of \(N,N\)-dimethyl-3-oxa-glutaramic acid has been studied in the present paper.

2 Experimental

2.1 Materials

\(N,N\)-dimethyl-3-oxa-glutaramic acid was prepared according to ref. [4]. It was crystallized twice from water to gain the purity of 99.9%. The crystalline compound was then dried in a vacuum desiccator at room temperature for one month.

2.2 Procedure

A DOTA sample was dissolved in D\(_2\)O and its \(^1\)H-NMR spectrum was obtained using a Bruker DMX-300. The infrared spectra of the solid sample were recorded on a Nicolet NEXUS 479 FT-IR spectrophotometer in the...
range of 4000-400 cm$^{-1}$ by using KBr discs. The contents of C, H and N elements were determined by a Perkin-Elmer microelement analyzer model 2400.

Thermogravimetry differential thermogravimetry (TG-DTG) curves were measured using a TA2100 thermobalance under the air atmosphere. The heating rate was set at 2.5, 5, 10, 15, and 20$^\circ$C·min$^{-1}$, respectively. The gaseous products of the TG experiments under the heating rate of 5$^\circ$C·min$^{-1}$ were blown with high-purity N$_2$ prior to the Nicolet NEXUS 670 FT-IR spectrophotometer for analysis.

![Figure 1](image1.png)

Figure 1 The structural formula of N,N-dimethyl-3-oxa-glutaramic acid.

### 3 Results and discussion

#### 3.1 Characterization

$^1$H-NMR of the purified compound: 2.71 (6H, $-N(CH_3)_2$), 4.03 (2H, $-OCH_2CON(CH_3)_2$), 4.18 (2H, $-OCH_2COOH$), 4.68 (2H, H$_2$O). The main FT-IR absorption peaks: 3415 cm$^{-1}$ (H$_2$O), 1721 cm$^{-1}$ (υ(C==O), carbonyl group 1), 1642 cm$^{-1}$ (υ(C==O), carbonyl group 2 (see Figure 1)), 1054 cm$^{-1}$ (υ(—O—)). The results of $^1$H-NMR and FT-IR analysis imply that the title compound has crystal water. The results of C, H and N elemental analyses (C, 40.54%, H, 7.58%, N, 7.82%) are in good agreement with the formula of the title compound containing one crystal water molecule (C$_6$H$_{13}$O$_5$N, C, 40.22%, H, 7.62%, N, 7.88%). Accordingly, it can be concluded that N,N-dimethyl-3-oxa-glutaramic acid is accompanied with one crystal water.

#### 3.2 Thermal decomposition mechanism

The typical TG-DTG curves for the title compound at a heating rate of 5$^\circ$C·min$^{-1}$ are shown in Figure 2. The appearance of two peaks in the DTG curve suggests that the thermal decomposition process of the title compound should occur in two steps. The TG curve shows a two-stage mass loss process.

![Figure 2](image2.png)

Figure 2 TG-DTG curves for the title compound at a heating rate of 5$^\circ$C·min$^{-1}$.

The first-stage started at about 50$^\circ$C and completed at 90$^\circ$C accompanied with 10.98% mass loss. This mass loss matches the theoretical value of the mass loss of one crystal water (10.06%). The second-stage began at about 150$^\circ$C and ended at 250$^\circ$C. The dehydrated compound was decomposed completely in this step.

In order to understand the second-stage decomposition process, the decomposition products in the temperature range of 150–260$^\circ$C were examined by using a FT-IR spectro-photometer. The infrared analysis of the title compound during the second-stage decomposition was carried out by choosing several typical temperatures (180, 200, 220, 240, and 250$^\circ$C). The results show the similar characteristic absorption peaks (see Figure 3),