*Journal of Thermal Analysis and Calorimetry, Vol. 94 (2008) 2, 529–534*

# HEAT CAPACITIES AND THERMODYNAMIC PROPERTIES OF *TRANS*-(*R*)-3-(2,2-DICHLOROETHENYL)-2,2-DIMETHYLCYCLOPROPANECARBOXYLIC ACID

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The heat capacities of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid in the temperature range from 78 to 389 K were measured with a precise automatic adiabatic calorimeter. The sample was prepared with the purity of 0.9874 mole fraction. A solid–liquid fusion phase transition was observed in the experimental temperature range. The melting point, $T_m$, enthalpy and entropy of fusion, $\Delta_{fus}H_m$, $\Delta_{fus}S_m$, were determined to be 344.75±0.02 K, 13.75±0.07 kJ $mol^{-1}$, 39.88±0.21 J $K^{-1}$ $mol^{-1}$, respectively. The thermodynamic functions of the sample, $H_{(T)}–H_{(298.15)}$, $S_{(T)}–S_{(298.15)}$ and $G_{(T)}–G_{(298.15)}$, were reported with a temperature interval of 5 K. The thermal decomposition of the sample was studied by TG analysis, the thermal decomposition starts at ca. 421 K and terminates at ca. 535 K, the maximum decomposition rate was obtained at 525 K. The order of reaction, pre-exponential factor and activation energy, are $n$=0.14, $A$=1.15·$10^8$ $min^{-1}$, $E$=66.27 kJ $mol^{-1}$, respectively.

***Keywords:*** *adiabatic calorimetry, heat capacity, thermal decomposition, thermodynamic function, trans-(R)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid*

## Introduction

*Trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid is one of the important intermediate of the preparation of fenpropathrin pesticide, many kinds of high performance and activity fenpropathrin pesticide such as permethrin, alphamethrin, cyfluthrin, fenpyrithrin, etc., are synthesized with it [1–3]. Its formula is $C_8H_{10}O_2Cl_2$ and its structure as follow.

The compound has four isomers, the two isomers, *cis*-(*R*)- and *trans*-(*R*)- 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid, can be used as the materials to synthesize fenpropathrin pesticides, but the other two isomers, *cis*-(*S*)- and *trans*-(*S*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid are useless for the synthesis of fenpropathrin pesticide [1, 2].

The thermodynamic data is one of the important basis of improving the synthesis process of fenpropathrin pesticide and studying on the reaction mechanism, and calorimetry is one of the effectual method for these research [4–6]. Stereoselective synthesis, separating the isomers of product and intermediates can reduce the using amount of insecticide, improving economic performance and decrease environmental pollution.

The heat capacities and thermodynamic data are the important basis of improving the stereoselective synthesis process, purifying and separating the isomers of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid. The research was aimed at obtaining the important thermodynamic data of the compound, and studying its thermodynamic properties. These results will be the important basis of improving the preparation method, increasing the economic performance and decreasing the environmental pollution.

The heat capacities of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid of high purity (0.9874 molar fraction) was measured in temperature range between 78 and 389 K with an automatic adiabatic calorimeter in this work. At the same time, the melting point, $T_m$, enthalpy and entropy of fusion, $\Delta_{fus}H_m$, $\Delta_{fus}S_m$, were calculated. The thermal decomposition of the sample was studied by thermogravimetric (TG) analytic technique.

## Experimental

### *Sample preparation*

3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid was prepared by the hydrolysis of

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*1388–6150/$20.00*

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3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-carboxylic ester after the reaction of 1,1-dichloro-4-methyl-1,3-pentadiene and diazoacidic ester [1]. The crystal product of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropanecarboxylic acid was separated and purified [7]. Finally, the sample was obtained. The molecular structure was verified with NMR (model: Bruker DRX-400). The purity of the sample was determined to be 98.74% (molar fraction) by HPLC (model: Shimazu 10A) [7].

### *Methods*

#### Adiabatic calorimetry

The heat capacity measurements were carried out with an automatic calorimeter over the temperature range 80 to 400 K. The equipment was based on the Nernst step heating method. The adiabatic calorimeter was described before in detail [8–10] and only the major features of the equipment are described here.

The calorimeter consists of a calorimeter cell, an adiabatic shield, a guard shield, two sets of differential thermocouples, and a vacuum can. In order to obtain good adiabatic conditions between the calorimeter and its surroundings, two adiabatic shields were used to resist the heat transfer between the cell and its environment. The cell and two shields were housed in a high vacuum can and immersed in a liquid nitrogen cryostat. The principle of the automatic adiabatic control circuits were described in [9].

The uncertainty temperature between the outer edges of the vanes and the sample cell was less than 1 mK in the determination of heat capacity, and the temperature change of the sample cell in the equilibrium period was in the range of 0.1–0.05 mK min$^{-1}$.

The energy introduced into the sample cell was supplied by a direct current supply with a stability of about 5 ppm. A computer-based on-line measuring system was designed which could automatically measure the current through the calorimeter heating wire, the voltage across it, the duration of energy input and then the introduced energy was obtained. In order to verify the reliability of the calorimeter, the molar heat capacities of $\alpha$-$Al_2O_3$ were measured from 80 to 400 K. The deviations of the experimental results from the smoothed curve lie within ±0.1%, while the inaccuracy was within ±0.2% compared with those [4] of the National Institute Science and Technology (formerly the National Bureau of Standards, NBS) in the whole temperature range.

The heating rate was controlled in the range of 0.2–0.4 K min$^{-1}$ while the sample in solid and liquid phase. The intervals of temperature rising was 2–4 K generally and the intervals was reduced a little while at the temperature of sample melting. The duration of heating was measured by means of a digitally displayed electronic timer–controller with an accuracy of 10$^{-3}$ s. The data were read and calculated automatically by a computer on the real time.

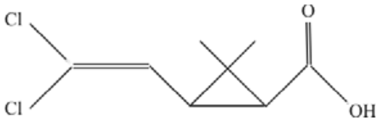

**Fig. 1** Molecular structure of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid

#### Thermogravimetry

Thermogravimetric analysis was performed with a TG 951 thermal balance in the temperature range 340–550 K. A nitrogen gas flow rate of 150 mL min$^{-1}$ and a heating rate of 3 K min$^{-1}$ were employed.

## Results and discussion

### *Heat capacity*

The experimental molar heat capacities of *trans*-(R)-3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropane carboxylic acid of a typical run are shown in Fig. 2 and listed in Table 1. In solid region the heat capacities of the sample were measured with 60 points in temperature range from 78 to 300 K and 13 points in liquid region between 351 and 389 K. In fusion region the heat capacities of the sample were determined with 26 points in temperature range from 300 to 350 K. No thermal anomaly was observed in solid and liquid regions, it demonstrates that the structure of the compound is stable in the temperature range. The values of heat capacities were fitted with the following polynomial expressions with least squares method.

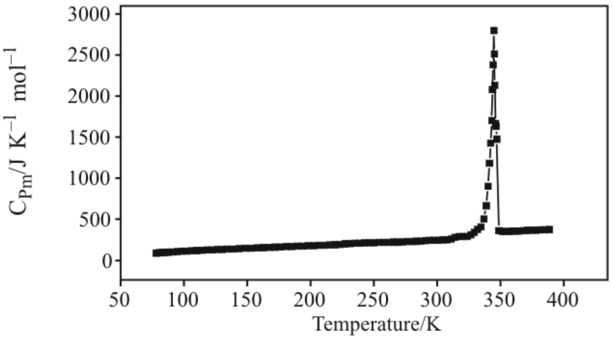

**Fig. 2** Heat capacity curve of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid

For solid region (78–300 K):

$$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})=173.588+76.771X+6.753X^2-18.3744X^3-12.075X^4+18.287X^5 \qquad (1)$$

where $X=(T-190)/110$ and $T$/K is temperature.

For liquid region (351–389 K):

$$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})363.113+14.843X-0.27996X^2-2.554X^3+0.18273X^4 \qquad (2)$$

where $X=(T-370)/19$ and $T$/K is temperature. The deviation of the experimental data from the smoothed values in whole regions is within ±0.2%.

*Melting point, enthalpy and entropy of fusion, purity determination*

To determine the melting point ($T_m$) and molar enthalpy ($\Delta_{fus}H_m$), a step heating method was used. It is based on the following principle. The sample was heated with a small amount of heat once and to measure the equilibrium temperature. The increment of the energy required to heat the sample from the temperature $T_1$, below the melting point, to the temperature $T_2$, above it, was measured. With multiple times heating, the melting point was approached and the

**Table 1** Experimental molar heat capacities of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropane carboxylic acid [$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})$]

| $T$/K | $\mathrm{C_{p,m}}$/J K$^{-1}$ mol$^{-1}$ | $T$/K | $\mathrm{C_{p,m}}$/J K$^{-1}$ mol$^{-1}$ | $T$/K | $\mathrm{C_{p,m}}$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|
| 78.2 | 87.6 | 202.6 | 180.4 | 323.6 | 292.0 |
| 79.3 | 92.9 | 206.8 | 183.0 | 326.6 | 310.3 |
| 80.4 | 92.98 | 211.0 | 185.8 | 329.5 | 341.0 |
| 81.5 | 92.8 | 215.1 | 188.6 | 332.1 | 376.6 |
| 82.9 | 95.9 | 219.2 | 191.3 | 334.6 | 410.5 |
| 84.7 | 98.9 | 223.2 | 194.0 | 336.9 | 505.1 |
| 87.5 | 100.7 | 227.3 | 202.2 | 338.8 | 665.9 |
| 91.2 | 104.4 | 231.2 | 204.7 | 340.3 | 903.6 |
| 94.9 | 107.8 | 235.1 | 208.6 | 341.4 | 1182.9 |
| 98.5 | 111.2 | 238.9 | 211.2 | 342.4 | 1425.3 |
| 102.0 | 114.2 | 242.7 | 213.5 | 343.2 | 1701.1 |
| 105.8 | 117.3 | 246.5 | 214.2 | 343.8 | 2081.1 |
| 110.1 | 120.8 | 250.3 | 216.0 | 344.3 | 2378.8 |
| 114.3 | 123.4 | 254.1 | 218.7 | 344.7 | 2797.3 |
| 118.4 | 126.9 | 257.8 | 219.1 | 345.1 | 2512.0 |
| 122.4 | 130.2 | 261.6 | 219.9 | 345.6 | 2130.6 |
| 126.3 | 132.6 | 265.3 | 221.6 | 346.1 | 1668.2 |
| 130.2 | 134.9 | 269.0 | 223.6 | 346.61 | 1629.9 |
| 134.1 | 137.5 | 272.6 | 225.7 | 347.2 | 1475.9 |
| 138.5 | 140.7 | 276.3 | 227.9 | 348.7 | 363.4 |
| 143.5 | 143.9 | 279.9 | 230.5 | 351.4 | 351.1 |
| 148.4 | 147.0 | 283.5 | 233.3 | 354.1 | 351.74 |
| 153.2 | 149.8 | 287.0 | 236.1 | 356.8 | 353.4 |
| 158.0 | 153.1 | 290.5 | 239.2 | 359.5 | 355.58 |
| 162.6 | 156.3 | 293.9 | 243.3 | 362.2 | 357.38 |
| 167.3 | 159.2 | 297.5 | 243.0 | 364.9 | 358.8 |
| 171.9 | 161.8 | 300.9 | 246.3 | 367.9 | 362.0 |
| 176.4 | 164.7 | 304.3 | 248.7 | 371.3 | 364.5 |
| 180.9 | 167.3 | 307.7 | 250.5 | 374.7 | 366.5 |
| 185.3 | 170.1 | 311.1 | 260.6 | 378.1 | 368.2 |
| 189.7 | 172.8 | 314.3 | 282.1 | 381.5 | 372.2 |
| 194.1 | 175.3 | 317.4 | 289.5 | 384.8 | 373.6 |
| 198.4 | 177.9 | 320.5 | 290.7 | 388.7 | 375.0 |

enthalpy of fusion of the sample was derived by the following Eq. (3).

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = \frac{Q - n\int_{\mathrm{T_i}}^{\mathrm{T_m}} C_{\mathrm{p,m(S)}}\mathrm{d}T - n\int_{\mathrm{T_m}}^{\mathrm{T_f}} C_{\mathrm{p,m(L)}}\mathrm{d}T - \int_{\mathrm{T_i}}^{\mathrm{T_f}} H_0\mathrm{d}T}{n} \tag{3}$$

Summing up increments of the heat capacity in the melting region with corrections for lattice heat capacity from temperature $T_1$ to $T_{\mathrm{m}}$, and for heat capacity of liquid from $T_{\mathrm{m}}$ to $T_2$, where, $n$ is the molar number of the sample; $Q$, the total amount of heat introduced into the sample; $C_{\mathrm{p,m(S)}}$, $C_{\mathrm{p,m(L)}}$, $H_0$, the heat capacity of sample in solid and liquid state and heat capacity of empty cell. The entropy of fusion $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ of *trans*-R-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylic acid was derived by combining the enthalpy and melting point.

During the heat capacity experiment, we found that the temperature of fusion from solid phase to liquid took place from about 300 to 360 K. The determination of temperature of fusion $T_{\mathrm{m}}$ and enthalpy of fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ for the sample was carried out from three series of heat capacity measurements in this temperature range. The three runs of experimental and calculated results are listed in Table 2. The averaged melting point $T_{\mathrm{m}}$ was determined to be 344.75±0.02 K, the averaged enthalpy $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ was 13.75±0.07 kJ mol$^{-1}$, and the averaged entropy $\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ was $\Delta_{\mathrm{fus}}S_{\mathrm{m}}=\Delta_{\mathrm{fus}}H_{\mathrm{m}}/T_{\mathrm{m}}=39.9\pm0.2$ J K$^{-1}$ mol$^{-1}$.

The purity of the sample is determined based on a fractional melting method. The values of melting temperatures in the solid-liquid two-phase region are determined at a series of fraction melting. The basic principle is as the following. At the temperature several degrees below the melting point, an enough amount of energy is supplied to the sample cell for melting a small fraction of the sample, and the melting temperature is observed until equilibrium is reached. Following the attainment of equilibrium, another amount of energy is supplied to the sample and another portion of sample is melted, and a second equilibrium melting temperature observed. In this way, the values of melting temperatures in the solid-liquid two-phase region are determined at a series of fraction melted. Then the sample is completely melted and a final equilibrium temperature a few degrees above the melting point are determined. With the plot of equilibrium temperatures $T$/K *vs.* melting fractions, the melting points of sample and pure substance could be obtained. Then, the purity of the *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylic acid sample can be obtained according to the following Van't Hoff equation (4).

$$T_0 - T_{\mathrm{m}} = \frac{RT_0^2x}{\Delta_{\mathrm{fus}}H_{\mathrm{m}}} \tag{4}$$

where $T_{\mathrm{m}}$ is the melting point of sample and $T_0$ is the melting point of pure compound. $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ is the molar melting enthalpy of purity, and $x$ is the molar fraction of impurity.

In the present study, the experimental and calculated results are shown in Table 3 and Fig. 3. In Table 3, $Q$ is the amount of heat introduced into the sample for melting the respectively fraction sample F. With Fig. 3, extrapolating the equilibrium temperatures *vs.* inverse of melting fraction (1/F, F is melting fraction) to zero, the melting point of pure 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylic acid was obtained to be $T_0$=345.8 K. The purity of the sample was determined to be 98.56 mol%, it is very closed to 98.74 mol% obtained by HPLC. The result of purity determination demonstrated that calorimetry is an efficient method for the determination of high purity samples, and the method is simple and convenient for the purity determination.

**Table 2** Experimental and calculated results of temperature of fusion and enthalpy

| $T_{\mathrm{i}}$/K | $T_{\mathrm{f}}$/K | $T_{\mathrm{m}}$/K | $Q$/J | $\int_{\mathrm{T_i}}^{\mathrm{T_f}} H_0\mathrm{d}T/n$ | $n\int_{\mathrm{T_i}}^{\mathrm{T_m}} C_{\mathrm{p,m(S)}}\mathrm{d}T$ | $n\int_{\mathrm{T_m}}^{\mathrm{T_f}} C_{\mathrm{p,m(L)}}\mathrm{d}T$ | $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| 300.9 | 351.4 | 344.8 | 4233.5 | 1063.7 | 1361.6 | 264.5 | 13.8 |
| 302.6 | 352.7 | 344.7 | 4249.3 | 1057.2 | 1309.0 | 320.3 | 13.7 |
| 303.4 | 351.9 | 344.7 | 4158.3 | 1020.6 | 1284.6 | 284.4 | 13.7 |

**Table 3** Experimental results of purity measurement

| $Q$/J | 291.45 | 368.50 | 470.53 | 614.11 | 813.94 | 1104.5 | 1566.7 |
|---|---|---|---|---|---|---|---|
| $F=Q/(\Delta H_{\mathrm{m}}n)$ | 0.18566 | 0.23474 | 0.29974 | 0.39120 | 0.51850 | 0.70358 | 0.99804 |
| $1/F$ | 5.3861 | 4.2600 | 3.3363 | 2.5562 | 1.9286 | 1.4213 | 1.0020 |
| $T$/K | 340.28 | 341.43 | 342.38 | 343.18 | 343.82 | 344.34 | 344.77 |

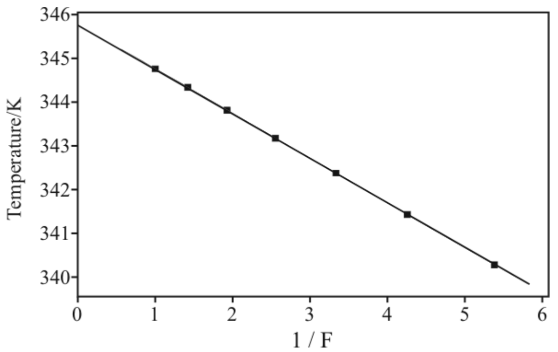

**Fig. 3** Equilibrium temperature *vs.* inverse of melting fraction; · – experimental data; — – linear fit of data

### Thermodynamic functions of the sample

The heat capacity near thermodynamic zero point was difficult to obtain in the present experiment condition. Therefore, only the thermodynamic function data in temperature range from 298.15 to 400 K were given based on standard state (298.15 K). The data of thermodynamic function was calculated by the following equations and the results, $H_{m(T)}-H_{m(298.15)}$, $S_{m(T)}-S_{m(298.15)}$ and $G_{m(T)}-G_{m(298.15)}$ are listed in Table 4.

$$H_{m(T)}-H_{m(298.15)}=\int_{298.15}^{T}C_{p,m}\,dT \qquad (5)$$

$$S_{m(T)}-S_{m(298.15)}=\int_{298.15}^{T}(C_{p,m}/T)\,dT \qquad (6)$$

$$G_{m(T)}-G_{m(298.15)}=\int_{298.15}^{T}C_{p,m}\,dT-T\int_{298.15}^{T}(C_{p,m}/T)\,dT \qquad (7)$$

### Heat decomposition

The heat decomposition of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane carboxylic acid was determined with a thermobalance (Model TG 951) in nitrogen atmosphere. The results are shown in Fig. 4. It can be seen from the TG-DTG curves in Fig. 4 that there is only one mass lose activity in the whole temperature range. The decomposition started from about 421 and ended at 535 K. The decomposition peak temperature obtained from the DTG curve was 525 K. The decomposition reaction kinetic parameters can be obtained by processing TG data [11]. The order of reaction, pre-exponential factor, and activation energy are $n$=0.14, $A$=1.15·10$^{8}$ min$^{-1}$ and $E$=66.27 kJ mol$^{-1}$, respectively.

**Table 4** Calculated thermodynamic function data of the sample

| $T$/K | $C_{p,m}$/J K$^{-1}$ mol$^{-1}$ | $H_{m(T)}-H_{m(298.15)}$/kJ mol$^{-1}$ | $S_{m(T)}-S_{m(298.15)}$/J K$^{-1}$ mol$^{-1}$ | $G_{m(T)}-G_{m(298.15)}$/J mol$^{-1}$ |
|---|---|---|---|---|
| 298.15 | 243.6 | | | |
| 300 | 245.6 | 452.8 | 1.5 | –1.7 |
| 305 | 249.6 | 1687.8 | 5.6 | –19.2 |
| 310 | 258.3 | 2955.8 | 9.7 | –56.7 |
| 315 | 383.5 | 4307.8 | 14.1 | –117.9 |
| 320 | 389.6 | 5737.5 | 18.6 | –198.5 |
| 325 | 295.3 | 7197.8 | 23.1 | –303.2 |
| 330 | 345.4 | 8797.8 | 28.0 | –429.0 |
| 335 | 415.4 | 10697.8 | 33.7 | –581.6 |
| 340 | 903.2 | 13992.8 | 43.4 | –766.6 |
| 344.8 | maximum | | | |
| 350 | 365.5 | 29336.8 | 87.9 | –1438.7 |
| 355 | 351.3 | 31126.8 | 93.0 | –1891.7 |
| 360 | 356.5 | 32894.3 | 98.0 | –2367.7 |
| 365 | 359.2 | 34683.6 | 102.9 | –2869.8 |
| 370 | 363.1 | 36489.5 | 107.8 | –3396.5 |
| 375 | 367.0 | 38314.7 | 112.7 | –3947.8 |
| 380 | 370.5 | 40158.3 | 117.6 | –4523.6 |
| 385 | 373.4 | 42018.2 | 122.4 | –5123.5 |
| 390 | 375.7 | 43891.0 | 127.3 | –5748.2 |
| 395 | 376.9 | 45772.4 | 132.1 | –6396.4 |
| 400 | 376.9 | 47657.0 | 136.8 | –7068.6 |

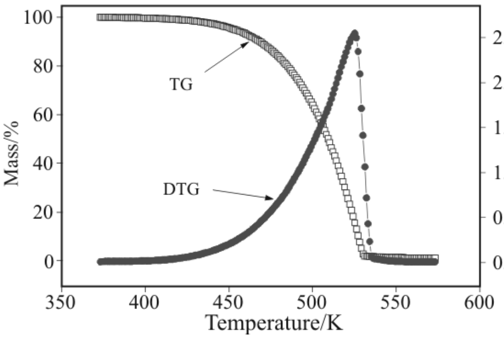

**Fig. 4** TG and DTG plots of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid in $N_2$ atmosphere

## Conclusions

The heat capacities of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclo-propanecarboxylic acid were measured with a precise automatic adiabatic calorimeter. The heat capacity curve shows that there is a phase change from solid to liquid phase in the temperature range from 300 to 360 K. The values of heat capacities were fitted with polynomial expressions in the temperature range of 78 to 300 K for solid phase (Eq. (1)) and in the temperature range of 351 to 389 K for liquid phase (Eq. (2)). The deviation of the experimental data from the smoothed values in whole regions is less than 0.2%.

The solid-liquid fusion phase transition was observed in the experimental temperature range. The melting point, $T_m$, enthalpy and entropy of fusion, $\Delta_{fus}H_m$, $\Delta_{fus}S_m$, were determined to be 344.75±0.02 K, 13.75±0.07 kJ $mol^{-1}$, 39.88±0.21 J $K^{-1}$ $mol^{-1}$, respectively. The thermodynamic functions of the sample, $H_{(T)}-H_{(298.15)}$, $S_{(T)}-S_{(298.15)}$ and $G_{(T)}-G_{(298.15)}$, were reported with a temperature interval of 5 K.

The purity of the sample is determined based on a fractional melting method. The result of purity determination demonstrated that calorimetry is an efficient method for the determination of high purity samples.

The thermal decomposition of *trans*-(*R*)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid was studied by TG analysis, the thermal decomposition starts at ca. 421 K and terminates at ca. 535 K, the maximum decomposition rate was obtained at 525 K. The order of reaction, pre-exponential factor and activation energy, are $n$=0.14, $A$=1.15·$10^8$ $min^{-1}$, $E$=66.27 kJ $mol^{-1}$, respectively.

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Received: December 10, 2007
Accepted: May 29, 2008
OnlineFirst: September 20, 2008

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DOI: 10.1007/s10973-007-8259-5