Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 451 (2006) 94–98
thermochimica acta
www.elsevier.com/locate/tca

Kinetics of the thermal decomposition of diethyldithiocarbamato tellurium (IV)

Shun Wang [a,b,*], Fan Chen [a], Shaoming Huang [a], Ruwang Liu [a], Juanjuan Lin [a]

[a] *Nano-materials & Chemistry Key Laboratory, Wenzhou University, Wenzhou 325027, PR China*
[b] *College of Chemical Engineering, China University of Mining and Technology, Xuzhou, Jiangsu 221008, PR China*

Received 17 June 2006; received in revised form 15 August 2006; accepted 5 September 2006

Abstract

The thermal decomposition of diethyldithiocarbamato tellurium (IV) (TDEC) is investigated by simultaneous TG/DTG/DSC-FTIR method in nitrogen atmosphere. Experimental results indicate that the TDEC decomposition goes through two stages, namely, the initial elimination of C_2H_5–N=C=S, S and $C_2H_5$with a molar ratio of 1:3:3, and the subsequent loss of CS_2, $N(C_2H_5)_2$ and C_2H_5–N=C=S with a molar ratio of 1:1:2. The trustworthy model-free kinetic approach has been used for characterization of the nonisothermal decomposition of TDEC. Our study shows that the activation energy for the two stages decomposition of TDEC greatly depends on the extent of conversion, implicating that the pyrolysis of TDEC features multi-step characteristics.

Keywords: Diethyldithiocarbamato tellurium (IV); Nonisothermal kinetics; Thermal decomposition mechanism

1. Introduction

As a class of both industrially and biologically significant chemicals, dithiocarbamates (DTCs) have widely been used, for example, as vulcanization accelerators and antioxidants in rubber industry [1], as pesticides and fungicides in agriculture and cosmetics [2,3], as anti-alcoholic drug [4,5] and tuberculostatic [6] in medicine, and recently as co-adjuvant in AIDS treatment [7]. In biological systems, DTCs are reported to be immunorestorative [8] and/or myeloprotective [9,10]. Besides the above benefits, various adverse effects [11,12], including neurobehavioral abnormalities [13], cutaneous anaphylaxis [14], immunosuppression [15], bone marrow and hematopoietic toxicity [11], have also been testified to interrelate with DTC exposure. In addition, DTCs are known to be inhibitors of nuclear factor-kB (NF-kB) [16,17] in a variety of cell including T lymphocytes [18,19], monocytes [20] and HL60 cells [21]. Those earlier studies have suggested the DTC-induced beneficial or toxic effects go through three possibilities, namely, metal chelation, enzyme alterations (both inhibition and induction) and disruptions in reduced glutathione homeostasis and/or changes in the redox status of the cell *via* anti-oxidant/pro-oxidant activity [11].

Among DTCs, diethyldithiocarbamato tellurium (IV), TDEC, is a powerful accelerator for natural rubber and most synthetic elastomers such as styrene butadiene rubber (SBR), nitrile butadiene rubber (NBR), ethylene–propylene–diene monomer (EPDM) and butyls. Although it is regarded as relatively harmless due to its low acute toxicity to mammals, adverse physiological effects are nevertheless observed. In a study on the development of chicken eggs, for example, TDEC is reported to cause increased early and late death rates as well as an increased incidence of malformations [22]. Conceivably, tellurium diethyldithiocarbamate could be broken down into tellurium and carbon disulphide (CS_2), both of which have been reported to produce teratogenic effects in biological systems [23]. Meanwhile, the organic part of TDEC, diethyldithiocarbamate, is also found to enhance the toxicity of other substances such as 1-methyl-4-phenyl-1,2,3,6-tetra-hydropyridine (MPTP) [24].

The widespread use and the increasing quantities of DTCs being released into the environment warrant that further understanding on the issues of DTCs degradation [25] and their impacts on physiological and environmental aspects should be

---

[*] Corresponding author. Fax: +86 577 88373064.
E-mail address: shunwang@wzu.edu.cn (S. Wang).

0040-6031/$ – see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.tca.2006.09.003

achieved. It is well known that tellurium diethyldithiocarbamate could be broken down with the formation of tellurium and carbon disulphide (CS_2), however, surprisingly little is known about its thermal decomposition kinetics. To understand the thermal decomposition property and decomposition kinetics is of significance in selectively manipulating decomposition products of TDEC.

In this paper, we focused our efforts on the thermal stabilities of DTEC under nonisothermal conditions by a simultaneous TG/DTG/DSC-FTIR method and its thermal decomposition kinetics. Our study illustrates that the activation energies of the two stages decomposition of TDEC greatly depend on the extent of conversion.

2. Experimental

The commercial grade diethyldithiocarbamato tellurium (IV) (TDEC) from Zhejiang Ultrafine Powders & Chemicals Co., Ltd. (China) was recrystallized twice from high-purity chloroform prior to its use. The simultaneous TG/DTG/DSC measurements were performed with a Netzsch STA 409C thermoanalyser under nitrogen atmosphere. Throughout this study the flow of nitrogen gas was fixed at 100 mL min^{-1} and the heating rate was at 5, 8, 10, 12, and 15 °C min^{-1}, respectively. Samples of 6.0–8.0 mg TDEC were placed in a Al_2O_3 crucible. The gaseous thermal decomposition products were followed and analyzed by a Nicolet Avatar 470 FT-IR spectrometer.

3. Results and discussion

3.1. Thermal decomposition of TDEC

Fig. 1 presents the typical TG, DTG and DSC curves measured at a heating rate of 10 °C min^{-1}. The DSC curve, obtained over a temperature range of 50–500 °C, illustrates that there are four principal endothermic processes, in which the first endothermic process spans the temperature range between 100 and 185 °C with the maximum at 111.2 °C. As is indicated by the TG curve, during the first endothermic process there is nearly no mass loss, implicating that this process is dominated by the melting of TDEC. In addition, our experiments show that the peak temperature (T_p) increases continuously with the heating rate β, in which a linear relationship is achieved. The second endothermic process (185.2–226.1 °C) with the peak temperature at 208.9 °C governs about 36.65% of the total mass loss. As is illustrated by the real time FT-IR spectra of the off-gases (see Figs. 2 and 3), a small amount of ethyl isothiocyanate (C_2H_5–N=C=S) with absorption bands at 2068 and 2047 cm^{-1} was authentically detected. The existence of alkylisothiocyanate has been confirmed in the decomposition processes of dialkyldithiocarbamato nickel (II) and copper (II) complexes [26]. Fig. 3 presents the corresponding evolution curve of C_2H_5–N=C=S as a function of temperature, which clearly shows that the production of C_2H_5–N=C=S begins at about 210.0 °C, slightly higher than the initial decomposition temperature (191.5 °C) of TDEC as found on the TG curve in

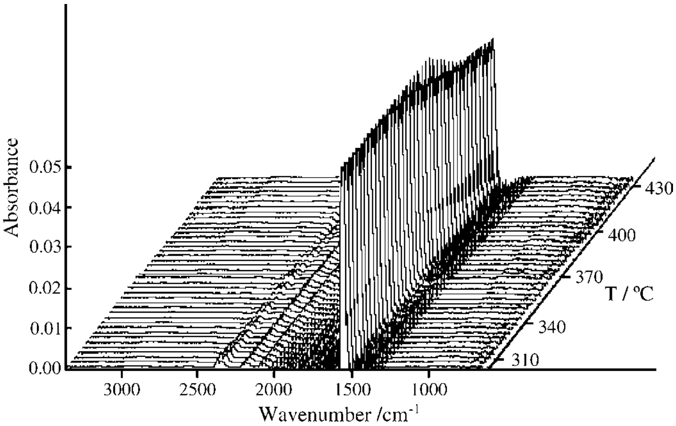


Fig. 2. Online FT-IR spectra of the off-gases of the pyrolysis of TDEC. All reaction conditions are the same as those in Fig. 1.

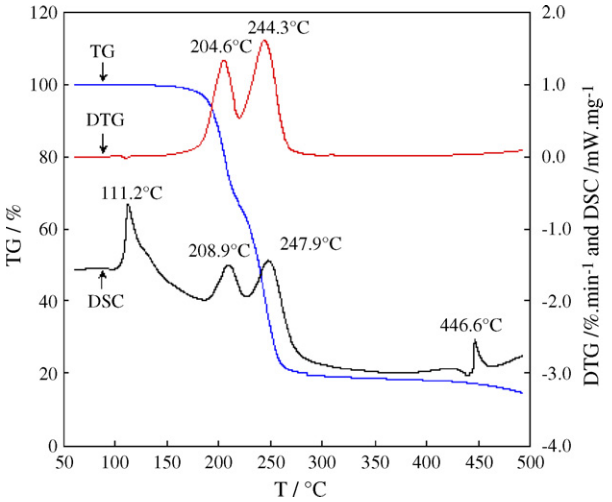


Fig. 1. TG/DTG/DSC curves of the thermal decomposition of TDEC. The flow rate of nitrogen is 100 mL min^{-1}. The heating rate equals 10 °C min^{-1} and the initial amount of TDEC is 6.20 mg.

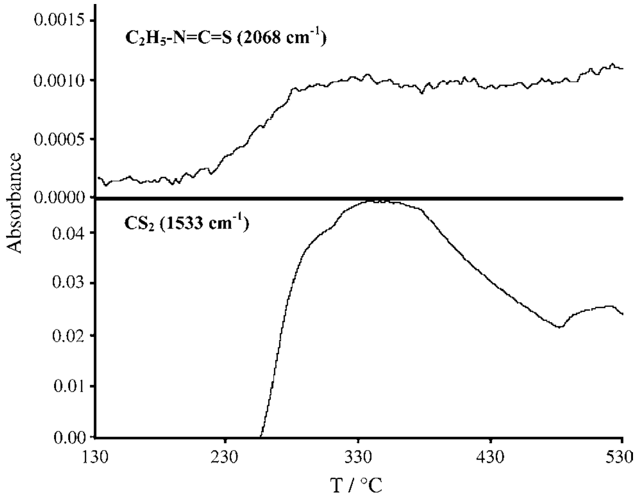
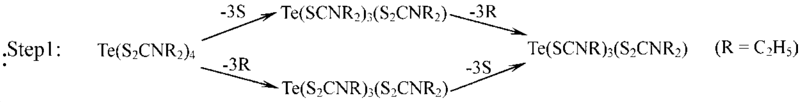


Fig. 3. The absorbance *vs.* temperature curves showing variations of concentrations of the thermal decomposition products as a function of temperature. Reaction conditions are listed in Fig. 1.

Fig. 1. Moreover, the decomposition rate of TDEC increases rapidly with respect to temperature and reaches a maximum at 204.6 °C (DTG curve). These experimental results suggest that the escape of C_2H_5–N=C=S is dominated by the following two steps [26]:

- Step 1:

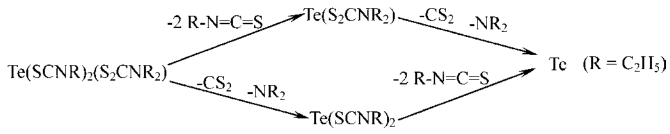


- Step 2:

$$Te(S_2CNR_2)(SCNR)_3 \xrightarrow{-R-N=C=S} Te(S_2CNR_2)(SCNR)_2, \quad (R = C_2H_5)$$

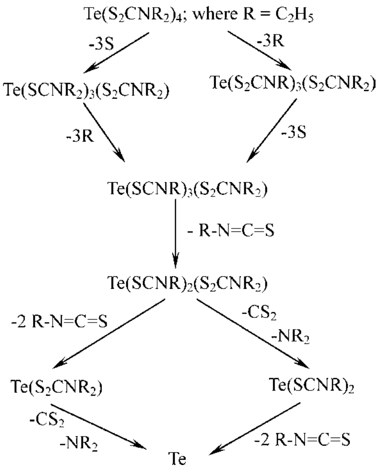
The step 1 involves the competing elimination processes of S and C_2H_5, in which C_2H_5 is likely a cation according to the earlier studies [26,27]. Based on the thermal analysis data, especially the real-time IR spectrum of off-gases, we believe that C_2H_5 cation is unstable and may form other stable species which cannot reach FT-IR spectroscope so that they are not registered by FT-IR. Another gaseous product, elemental sulfur, has no absorption bands in the range of IR spectrum. However, it is still unclear whether three sulfur groups are eliminated after three ethyl groups or vice versa. The step 2 includes the irreversible escape of C_2H_5–N=C=S which is confirmed by the IR absorption. Our observed mass loss of steps 1 and 2 is 36.32%, 35.26%, 36.65%, 35.62% and 34.31% at heating rate of 5, 8, 10, 12, and 15 °C min^{-1}, respectively, which is in good agreement with the theoretical calculation (37.45%). The above sequential elimination of S, C_2H_5 and C_2H_5–N=C=S (molar ratio equals 3:3:1) is also consistent with the fact that C_2H_5–N=C=S is detected at relatively high temperature ($T \geq 210$ °C). Similar experimental results were also reported in the pyrolysis of dithiocarbamato metal complexes [26,27]. The third endothermic process (226.1–300 °C) with the peak temperature at 247.9 °C exhibits a significant mass loss of 43.93%. The maximum decomposition rate reaches at 244.3 °C (see Fig. 1 DTG curve). As shown in the real time FT-IR spectra of the off-gases (see Fig. 3), there are two major species in the thermal decomposition products during this process, namely, CS_2 with absorption bands at 1533 and 2171 cm^{-1} and C_2H_5–N=C=S with absorption bands at 2068 and 2047 cm^{-1}. Carbon disulfide also has the same elution as the compound obtained from the decomposition of zinc dibenzyldithiocarbamate [28]. The evolution curve of CS_2 as a function of temperature (Fig. 3) shows that CS_2 starts to produce at ca. 245 °C and reaches the maximum concentration at about 325 °C. Notably, the production of CS_2 exhibits a minimum value at 474.4 °C. The theoretical production of tellurium (Te) is 17.7%, which is about 2% lower than the experimental result (19.61%). The thermal analysis data suggests that the production of tellurium be expressed as follows:

Step 3:



The step 3 involves the formation of tellurium by the competing eliminations of C_2H_5–N=C=S and $S_2CN(C_2H_5)_2$ which consists of two species, namely CS_2 and NR_2 anions [26]. NR_2 anions should be very active and may carry out very complex reactions. This may be the reason why NR_2 is not registered by FT-IR in the experimental temperature range. The final endothermic process at above 440 °C is characteristic of the melting of tellurium (m.p. 446.6 °C), which is in good agreement with the theoritical melting point (449.65 °C) measured in the air. As calculated from the data on the DSC, one can obtain the high purity (99.96%) tellurium through the pyrolysis of TDEC.

Based on the thermal analysis data, the detailed thermal decomposition scheme of TDEC may be represented as follows:



3.2. *Decomposition kinetics*

A model-free isoconversional method, developed by Flynn and Wall [29] and by Ozawa [30] has been frequently used in evaluating the activation energy of solid state reactions. Expressed in the natural logarithm form, the Flynn–Wall–Ozawa equation reads:

$$\log\beta = \log\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567\frac{E}{RT} \qquad (1)$$

where A is the pre-exponential factor, R the gas constant, E the activation energy, β the heating rate, α ($\alpha = \Delta W/\Delta W_\alpha$) the extent of conversion and T is the temperature. $G(\alpha)$ is an integral kinetic function. The activation energy related to a given conversion, $E_{\alpha,i}$, can be obtained by plotting $\log\beta_i$ as a function

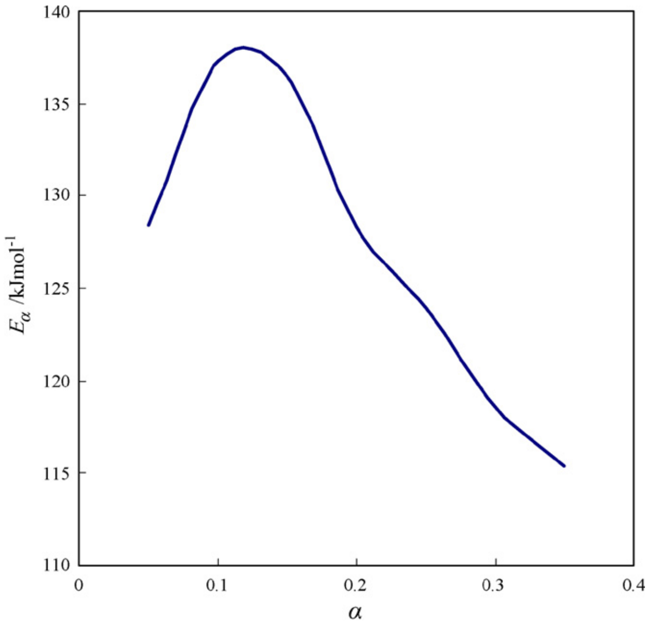


Fig. 4. Dependence of E_α on α for the second endothermic process of the thermal decomposition of TDEC.

of $T_{\alpha,i}^{-1}$. Figs. 4 and 5 reveal similar dependencies of $E_{\alpha,i}$ on α_i, namely, initially increasing and subsequently decreasing, both for the second and third endothermic processes of the decomposition of TDEC. Such a result implicates that the transformation of TDEC features multi-step characteristics. The shape of the dependence of E_α on α suggests that the kinetic scheme for the first decomposition process involves competing reactions (step 1) followed by an irreversible one (step 2) [31]. The step 1, involving the competing elimination processes of S and C_2H_5, at low conversions ($\alpha < 0.15$), can account for the initial increasing dependence of E_α on α, and the step 2, including the irreversible escape of C_2H_5–N=C=S, mainly contributes to the following decreasing dependence of E_α on α at relatively high conversions. In this study, for the second decomposition, the shape of dependence of E_α on α implies that such a process is likely arising from competing reactions followed by the consecutive escape of off-gases (step 3) [31]. A decreasing dependence of E_α on α is often encountered in solid decompositions which follow: solid → solid + gas. For example, similar dependence has been observed for the thermal decomposition of wood [32], $(NH_4)[VO(O_2)_2(NH_3)]$ [33] and for curing epoxy resins [34].

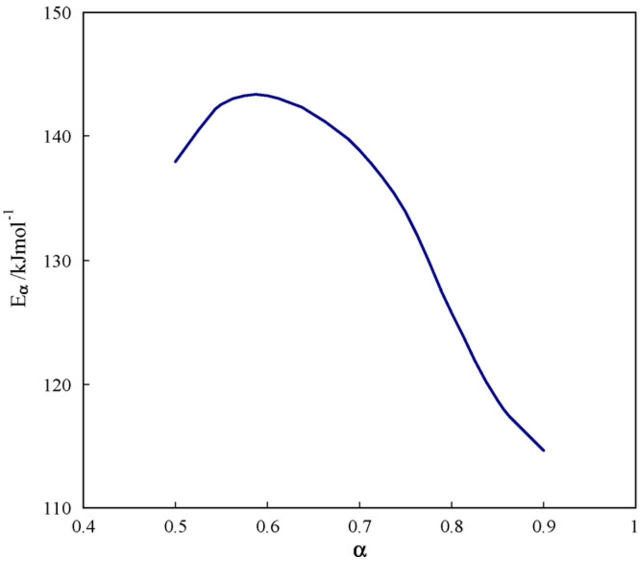


Fig. 5. Dependence of E_α on α for the third endothermic process of the thermal decomposition of TDEC.

4. Conclusions

The thermal decomposition of TDEC has been investigated under different heating rates. The real-time FT-IR spectra indicate that there are two major gas products, e.g., carbon disulfide ($CS_2(g)$) and ethyl isothiocyanate (C_2H_5–N=C=S). Our measurements show that TDEC decomposition goes through two stages: the first stage is dominated by the formation of intermediate $Te[S_2CN(C_2H_5)_2(SCN(C_2H_5))_3]$ through the competing loss of ethyl and sulfur groups. Such a process is followed by complete loss of C_2H_5–N=C=S. The second stage involves the formation of tellurium by the competing eliminations of $2C_2H_5$–N=C=S and $CS_2/N(C_2H_5)_2$. The detailed kinetic scheme for the thermal pyrolysis of TDEC is suggested to be as follows:

- Stage 1:

$$Te(S_2CNR_2)_4 \xrightarrow[-3S]{-3R} Te(S_2CNR_2)(SCNR)_3$$

$$\xrightarrow{-R-N=C=S} Te(S_2CNR_2)(SCNR)_2$$

- Stage 2:

$$Te(S_2CNR_2)_4(SCNR)_2 \xrightarrow[-CS_2,-NR_2]{-2R-N=C=S} Te, \quad (R = C_2H_5)$$

The energies of the two stages decomposition of TDEC are found to greatly depend on the extent of conversion. The understanding of the decomposition kinetics of TDEC is of significance in selectively manipulating decomposition products of TDEC for the benefits of industrial production, environmental protection and occupational safety and health.

Acknowledgements

We thank Prof. Jichang Wang and Prof. Vyazovkin for their useful discussions. This work is supported through NSFC (20471043, 20103010), Zhejiang Provincial Natural Science Foundation of China (Y404118) and the '151' Distinguished Person Foundation of Zhejiang Province of China.

References

[1] A. Hedenstedt, U. Rannug, C. Ramel, C.A. Wachtmeister, Mutat. Res. 68 (1979) 313–325.

[2] C.C. Lee, J.Q. Russell, J.L. Minor, J. Toxicol. Environ. Health 4 (1978) 93–106.
[3] A. Hulanicki, Talanta 14 (1967) 1371–1392.
[4] T. Kitson, Educ. Chem. 22 (1985) 43–45.
[5] M. Azzouz, P. Poindron, S. Guettier, N. Leclerc, C. Andres, J.M. Warter, J. Borg, J. Neurobiol. 42 (2000) 49–55.
[6] W. Weuffen, A. Kewitsch, Arch. Exp. Veterinaermed 21 (1967) 1049–1059.
[7] M.F. Rabbi, A. Finnegan, L. Al-Hartli, S. Stong, K.A. Roebuck, J. Acquir. Immun. Defic. Synd. Hum. Retrovirol. 19 (1998) 321–331.
[8] G.W. Brewton, E.M. Hersh, A. Rios, P.W.A. Mansell, B. Hollinger, J.M. Reuben, Life Sci. 45 (1989) 2509–2520.
[9] C.J. East, C.N. Abboud, R.F. Borch, Blood 80 (1992) 1172–1177.
[10] T.K. Schmalbach, R.F. Borch, Cancer Res. 49 (1989) 6629–6633.
[11] D.W. Pyatt, Y.Z. Yang, A. Le, W.S. Stillman, R.D. Irons, Biochem. Biophys. Res. Commun. 274 (2000) 513–518.
[12] A.G. Atanasov, S. Tam, J.M. Rǒcken, M.E. Baker, A. Odermatt, Biochem. Biophys. Res. Commun. 308 (2003) 257–262.
[13] D.B. Miller, Neurobehav. Toxicol. Teratol. 4 (1982) 779–787.
[14] E. Nettis, G. Assennato, A. Ferrannini, A. Tursi, Clin. Exp. Allergy 32 (2002) 441–447.
[15] E.L. Padgett, D.B. Barnes, S.B. Pruett, J. Toxicol. Environ. Health 37 (1992) 559–571.
[16] R.A. Neal, J. Halpert, Annu. Rev. Pharmacol. Toxicol. 22 (1982) 321–339.
[17] S. Orrenius, C.S.I. Nobel, D.J. Van den Dobbelsteen, M.J. Burkitt, A.F.G. Slater, Biochem. Soc. Trans. 24 (1996) 1032–1038.
[18] D.W. Pyatt, J. Gruntmeir, W.S. Stillman, R.D. Irons, Toxicology 128 (1998) 83–90.
[19] P. Brennan, L.A.J. O’Neill, Biochem. J. 320 (1996) 975–981.
[20] H.W.L. Ziegler-Heitbrock, T. Sternsdorf, J. Liese, B. Belohradsky, C. Weber, A. Wedel, R. Schreck, P. Bauerle, M. Strobel, J. Immunol. 151 (1993) 6986–6993.
[21] R. Bessho, K. Matsubara, M. Kubota, K. Kuwakado, H. Hirota, Y. Wakazono, Y.W. Lin, A. Okuda, M. Kawai, R. Nishikomori, T. Heike, Biochem. Pharmacol. 48 (1994) 1883–1889.
[22] A. Korhonen, K. Hemminki, H. Vainio, Teratog. Carcinog. Mutagen. 3 (1983) 163–175.
[23] C. Zenz, Occupational Medicine: Principles and Practical Applications, 2nd ed., Year Book Medical Publishers, Inc., Chicago, 1988, pp. 614–618.
[24] G.U. Corsini, S. Pintus, C.C. Chiueh, J.F. Weiss, I.J. Kopin, Eur. J. Pharmacol. 119 (1985) 127–128.
[25] J.O. Hill, S. Chirawongaram, J. Therm. Anal. 41 (1994) 511–518.
[26] B.F. Ali, W.S. A1-Akramawi, K.H. Al-Obaidi, A.H. Al-Karboli, Thermochim. Acta 419 (2004) 39–43.
[27] G. Barone, T. Chaplin, T.G. Hibbert, A.T. Kana, M.F. Mahon, K.C. Molloy, I.D. Worsley, I.P. Parkin, L.S. Price, J. Chem. Soc., Dalton Trans. (2002) 1085–1092.
[28] J.S. Helmick, W. Fiddler, J. Agric Food Chem. 42 (1994) 2541–2544.
[29] J.H. Flynn, L.A. Wall, J. Polym. Sci. Part B: Polym. Lett. 4 (1966) 323–328.
[30] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881–1886.
[31] S. Vyazovkin, Int. J. Chem. Kinet. 28 (1996) 95–101.
[32] S. Vyazovkin, Thermochim. Acta 223 (1993) 201–206.
[33] C.A. Strydom, D. de Waal, J. Therm. Anal. 38 (1992) 943–951.
[34] D.A. Ivanov, V.F. Chuvaev, M.R. Kiselev, J. Therm. Anal. 38 (1992) 1061–1070.