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Polymorphs of 2,4,5,6-tetrachloro-1,3-benzenedicarbonitile and their transformations

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Abstract

The transformation of Polymorphs (α and β modifications) of 2,4,5,6-tetrachloro-1,3-benzenedicarbonitile (chlorothalonil) to each other was studied by DSC method. The transformation temperature for α to β was determined to be $150.5 \pm 0.1\,^{\circ}\mathrm{C}$. The enthalpy, ΔH_t, and activation energy, E_a, for the transformation α to β were found to be, respectively, $4.03 \pm 0.03\,\mathrm{kJ\,mol^{-1}}$ (significance level = 0.02) and $6.5 \pm 0.9 \times 10^2\,\mathrm{kJ\,mol^{-1}}$ (95% confidence limits). The rate of transformation for α to β is fast, but the reverse is very slow. The X-ray powder diffraction (XRD) patterns of the two modifications were measured, and three of the strongest lines ($2\theta/^{\circ}$ and relative intensity (I/I_0)) for each modification are given, relatively, 25.52 (100), 14.38 (56), 27.95 (47); 26.58 (100), 14.33 (6), and 54.77 (3).

Keywords: Chlorothalonil; Polymorphs; Transformation; Activation energy; Enthalpy

1. Introduction

In order to design an acceptable solid dosage from a pesticide, it is necessary to know its inherent stability of the pesticide with respect to physical and chemical interactions, such as heat, light, solvent etc. The presence of unstable modifications of a pesticide affects the stability of its preparations under various environment factors. The crystal structure is crucial for the stability and effectiveness of pesticides and dosage forms. According to the second law of thermodynamics, in a condensed system under constant pressure except at the invariant point there is only one stable modification. Hence, it can be expected that the unstable modifications may give rise to the stability problems by transforming to the stable one during processing and storage. Thus, thorough understanding the modifications of a pesticide is important in the formulation of the pesticide products.

2,4,5,6-Tetrachloro-1,3-benzenedicarbonitile (chlorothalonil) was put on the market by Diamond Alkali Co. in 1963. It is a high efficient, low toxic and safe pesticide, and has been used extensively in agriculture and forestry as bactericide. At present, many preparations of chlorothalonil, e.g. powder, wettable powder, emulsion, oil soluble concentrate, aqueous suspension, etc. are on the market. However, little is known about its crystallography and polymorphism. In 1981, Doyle [1] published the crystal structure of chlorothalonil. Abe [2] disclosed that there are two modifications α and β, and α modification is stable at room temperature in 2001. In order to identify these modifications, the authors gave one XRD line for each modification [2]. In view of the importance of the stability of chlorothalonil, it is necessary to know about its polymorphs as detail as possible. The aim of this study was to determine the fundamental data, such as temperature of transformation, enthalpy, activation energy, XRD patterns and spontaneous periods of transformation.

2. Experimental

2.1. Materials

Chlorothalonil was obtained as commercial grade from Jiangyin Suli Fine Chemical Co. Fractional crystallization

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Table 1
Three of the most intense XRD reflections of α and β modifications

α Modification				β Modification			
Serial number	2θ/°	d (Å)	I/I_0	Serial number	2θ/°	d (Å)	I/I_0
11	25.52	3.488	100	08	26.58	3.351	100
02	14.38	6.155	56	02	14.33	6.176	6
13	27.95	3.190	47	24	54.77	1.675	3

was carried using analytical grade toluene as solvent and the product is α modification. The purity of α modification obtained is 99.5% by high performance liquid chromatography. The β modification was prepared by heating α modification at 180 °C for 2 h. The prepared β modification was coarse, granular, and slightly sintered crystalline, but not a melted solid. After a dry storage period at ambient conditions, transformation of β to α spontaneous processes completely (see Section 3.4). The XRD pattern of this spontaneous transformation product were same as α confirms this transformation. Both of the α and β modifications were identified by DSC and XRD methods.

2.2. Methods

In this study DSC analysis was carried out under dynamic and isothermal conditions in purge using extra pure nitrogen with a Perkin-Elmer Pyris 1 differential scanning calorimeter. The rate of nitrogen flow was 20 $\mathrm{cm}^3\,\mathrm{min}^{-1}$, and the mass of sample was taken ranging from 5.5 to 6.5 mg. The instrument was calibrated by using indium as standard. Closed aluminum cups were used as containers to prevent the mass loss due to sublimation of chlorothalonil.

The DSC curves were scanning generally from room temperature to 180 °C with heating rates 1.0, 2.5, 5.0, 7.5, 10.0, 12.5 and 15.0 °C min^{-1} This top temperature was chosen to ensure the complete transition from α to β. Values of the initial (T_i), extrapolated onset (T_e) and peak (T_p) temperatures of the endothermic peak were obtained from these DSC curves and were used for E_a calculation and ΔH_t determination.

In order to find the thermodynamic transition temperature of α to β modification, the following heating program was designed: samples of α modification were heated to 130 °C, 2 min, and then (a) with heating rate 10 °C min^{-1} to temperature, T and holding for a period t, (b) with cooling rate 10 °C min^{-1} to 145 °C, 2 min, (c) with heating rate 10 °C min^{-1} to 180 °C. The enthalpy, ΔH_p was obtained from these DSC curves.

XRD patterns were taken at room temperature with an X-ray diffractometer (D/MAX-2500, Rigaku Corporation, Japan). The operation conditions were K_α radiation, 45 KV, 200 ma, 0.02° 2θ step^{-1} from 10 to 60°, and scanning speed 8° 2θ min^{-1}. These data were measured in duplicated and the average values are listed in Table 1. Controlled temperature XRD was preformed with Reactor Chamber (XRK 900) and it is necessary accessories Temperature Control Unit (TCU 750) (Anton Paar, Austria). These data were measured are listed in Table 2.

2.3. Mathematical elaboration of DSC curves

The degree of transformation, D, defined as

$$D = \frac{\Delta H_t - \Delta H_\mathrm{p}}{\Delta H_t} \tag{1}$$

was calculated. ΔH_t is the enthalpy of α to β transformation and ΔH_p is the enthalpy obtained under the conditions of heating program at temperature, T and time, t.

The activation energy, E_a, for the transformation process was calculated using the Ozawa method

$$\frac{\mathrm{d}(\ln \Phi)}{\mathrm{d}(1/T_\mathrm{P})} = -\frac{E_\mathrm{a}}{R} \tag{2}$$

where E_a is the activation energy (kJ mol^{-1}), R is the gas constant (J mol K^{-1}), Φ is the linear heating rate (K min^{-1}) and T_P is the temperature (K) of the peak temperature of DSC curve [3,4].

Table 2
Controlled temperature XRD data of α to β transition

Serial number	Heating program and scanning	Peaks of α modification			Peaks of βmodification		
		25.52^{c}	14.38^{c}	27.95^{c}	26.58^{c}	14.33^{c}	54.77^{c}
1	(a) 10 °C min^{-1} from room temperature to 120 °C; (b) 2 °C min^{-1} from 120 to 146 °C scanning immediately	−0.24	−0.10	−0.29	^{a}	^{b}	^{a}
2	Rescanning after scanning of serial number 1 was completed	−0.24	−0.10	−0.29	^{a}	^{b}	^{a}
3	After scanning of serial number 2 was completed, (c) 2 °C min^{-1} from 146 to 162 °C scanning immediately	−0.30	^{b}	^{a}	−0.66	−0.33	−0.86
4	After scanning of serial number 3 was completed, isothermally 10 min at 162 °C scanning immediately	^{a}	^{b}	^{a}	−0.64	−0.31	−0.86
5	After scanning of serial number 4 was completed, isothermally 20 min at 162 °C scanning immediately	^{a}	^{b}	^{a}	−0.70	−0.35	−0.90

[a] Undetected. Detection limit of β < 0.1%; Detection limit of α < 2%.
[b] 2θ = 14.38 overlaps with 14.33°.
[c] Error at 2θ/°.

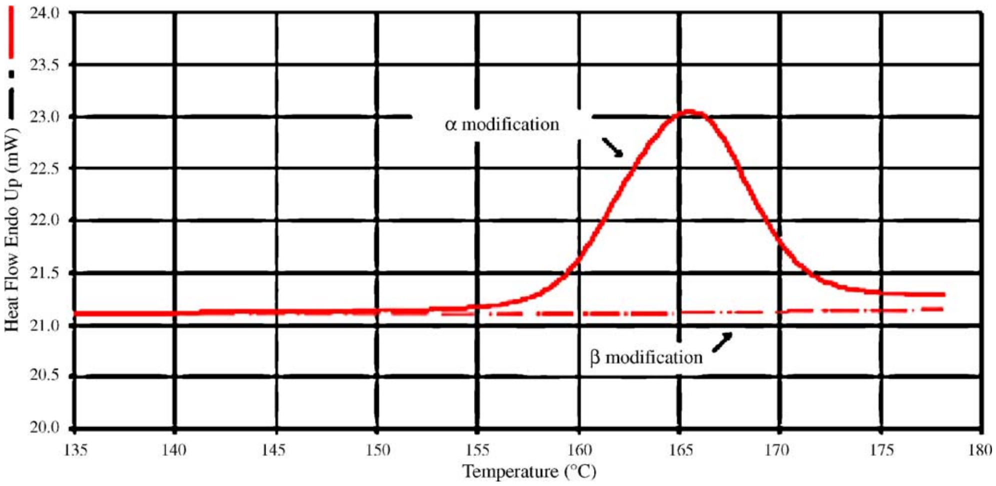

Fig. 1. DSC curves of α and β modifications.

3. Results and discussion

3.1. DSC curves and XRD patterns of modifications

Until quite recently, the XRD patterns of chlorothalonil were not found in the literature, except only one line for each of α ($2\theta = 25.5°$) and β ($2\theta = 26.4°$) modification was reported by Abe [2]. Three of the strongest lines for each modification are given in Table 1.

Fig. 1 shows the DSC scans of α and β modifications. An endothermic peak appears in the α modification, but not in the β. Fig. 2 shows the XRD patterns of α and β.

In order to prove the endothermic peak corresponding to the transition of α to β, use of a controlled temperature XRD to directly monitor the transition is preferred. Controlled temperature XRD data of α to β transition are shown in Table 2. It is given that transition of α to β does not process at 146 °C and fast at 162 °C. But unfortunately errors the 2θ errors of the three strongest lines for either α or β ranging from −0.10 to −0.90. Hence it is different to use a controlled temperature XRD to directly monitor the transition of α to β accurately. Chlorothalonil behaves relative high vapor pressure at temperature higher than ∼140 °C, the sublimation of chlorothalonil causes the specimen surface full of bumps and holes and the values of 2θ may not be measured accurately.

It is also preferred that use of room temperature XRD examination of a DSC sample recovered after scanning the sample just through the endothermic peak, because the mass of DSC sample recovered after scanning the sample only about 5 mg is not enough to prepare specimen for XRD scanning, the sample for X-ray diffractometer (D/MAX-2500) is greater than 100 mg and it is also difficult to be carried out.

Samples (about 200 mg in a closed vessel) were set into isothermal oven (166 ± 2 °C) and held a period ranging from

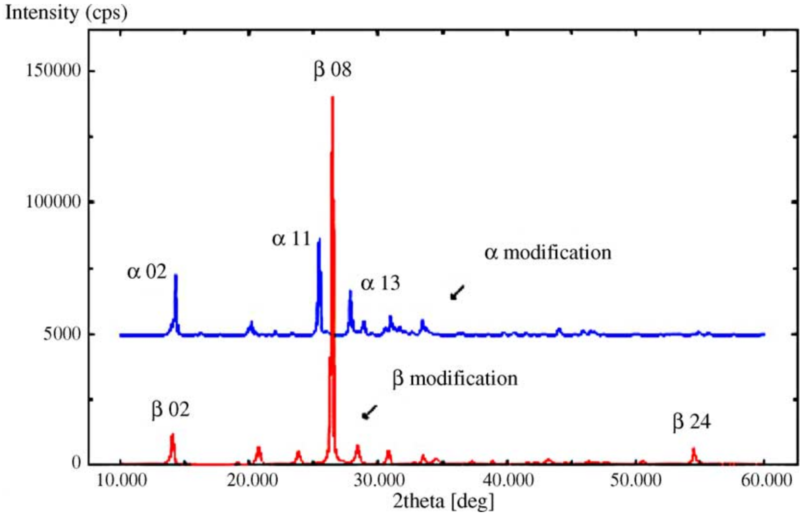

Fig. 2. X-ray powder diffraction patterns of α and β modifications.

5 to 20 min (the top temperature of the sample is less or equal to the oven temperature). In a period of 5 min, α and β modification coexist in the resulting sample; but α is not detected in a period of 10 min. The XRD pattern of the later resulting sample was same as prepared by heating α form at 180 °C for 2 h. The β form prepared by holding the α form at 180 °C (its melting point is 250 °C) for 2 h retains disperse crystalline state. Because the XRD pattern of the product of spontaneous transformation of β to α at ambient conditions is same as the β modification prepared by heating α modification at 180 °C for 2 h (see Section 3.4). All the above prove that the endothermic peak observed is a α to β solid state conversion and not the melting or degradation of α modification. Hence, the endothermic process is corresponding to the α to β transformation.

These data were used to identifying the two modifications.

3.2. *α to β transformation*

An endothermic peak from DSC curve of α modification is shown in Fig. 1, but not found from β modification. This was confirmed by scanning DSC curves of more than 10 samples for each of the two modifications. The DSC curves also shows that the transformation of α to β is a fast process. In order to determine the characteristic parameters of these two modifications, DSC curves with a series of heating rates were scanned, and the values of T_i, T_e, T_p and ΔH_t of each curve were listed in Table 2. Because DSC data possess program characteristics, determinations of these values with various heating rates were carried out. Regression equations of linear relation obtained were:

$$T_{\mathrm{i},\Phi} = 150.8 + 0.279 \times \Phi \qquad (3)$$

and

$$T_{\mathrm{i},\Phi} = 154.6 + 0.226 \times \Phi \qquad (4)$$

where $T_{\mathrm{i},\Phi}$ is the value of T_i at heating rate Φ and $T_{\mathrm{e},\Phi}$ is the value of T_e at heating rate Φ. In Eqs. (3) and (4), the correlation coefficient, *r*, is equal to 0.996 and 0.980, respectively, and thus these values are significant at the 1% level. According to these equations, by extrapolating to $\Phi = 0$, the values of $T_{\mathrm{i},0}$ (150.8 °C) and $T_{\mathrm{e},0}$ (154.6 °C) were obtained. The $T_{\mathrm{e},0}$ is 3.8 °C higher than $T_{\mathrm{i},0}$, and then $T_{\mathrm{i},0}$ is an approximation of the equilibrium temperature of transformation.

In order to increase the accuracy of the values of ΔH_t, expect the data listed in Table 2, additional seven determinations of the values of ΔH_t at heating rate 10 °C min^{-1} were carried out, the data: 14.99, 15.10, 15.13, 15.26, 15.28, 15.37 and 15.39 were obtained. Among the 15 data, data at heating rates 1.0 and 2.5 °C min^{-1} were deleted by Grubbs method (significant at the 0.5 and 2.5% level, respectively). In the view of these experiments, the heating rates were too low and the heating periods were too long, the mass loss introduced by sublimation may not be neglected. After deleting these data, the enthalpy, ΔH_t, was calculated to be 4.03 ± 0.03 kJ mol^{-1} (15.16 ± 0.12 J g^{-1}) and significance level is 0.02.

Table 3
Data of DSC curves of the endothermic peaks of α modification

Heating rate (°C min^{-1})	T_i (°C)	T_e (°C)	T_p (°C)	ΔH_t (J g^{-1})
1.0	151.1	154.7	156.50	13.31
2.5	151.6	155.0	158.11	14.52
5.0	152.1	155.8	159.43	15.00
7.5	152.7	156.6	161.13	15.23
10.0	153.4	156.7	161.57	14.99
10.0	153.5	156.9	161.49	15.33
12.5	154.3	157.0	162.32	14.91
15.0	155.1	158.1	163.02	15.13

It is possible to find the thermodynamic transforming temperature near $T_{\mathrm{i},0}$. After performing the above heating program, the data of α modification samples are listed in Table 3. From these data, thermodynamic temperature was found to be 150.5 ± 0.1 °C.

According to Eq. (2) and correlative data in Table 3, activation energy, E_a, was calculated to be $6.5 \pm 0.9 \times 10^2$ kJ mol^{-1} (95% confidence limits).

3.3. *β to α transformation*

DSC curves of sample β modification at different cooling rates were performed, and no exothermic peak was found. Several samples of β modification were held isothermally at temperature (*T*, °C) and retention (*t*, *h*) as follows: 147, 8; 148, 8; and 150, 4, β modification remained unchanged and α modification was not detected in all of these resulting samples by DSC method. The above data confirmed that the transformation of β to α is very slow, even near the transformation temperature.

3.4. *Spontaneous transformation of β to α during dry storage at ambient condition*

The spontaneous transformation of β to α modification during dry storage at ambient conditions was measured by XRD method. Although the transition of most samples were completed in various periods within 24 months, that is 2, 6, 12 or 24 months, but a few sample were found to be stable for more than 2 years. Typical data are shown in Table 4.

Table 4
Degree of α to β transformation under various conditions

Heating temperature *T* (°C)	Program *t* (min)	Temperature of sample (°C)	Transformation of α to β (D%)
151.50	30	150.431–150.455	0
151.70	10	150.687–150.692	4
151.40	20	150.514	13
152.00	20	150.8	18
154.00	10	152.9	31
156.00	20	154.9	100

Table 5
Spontaneous transformation of β to α during dry storage at ambient conditions

Storage period β coexist with α, month	Storage period* β undetected, month
–	2
2	6
6	12
12	24
24	–

* Detection limit of $\beta < 0.1\%$.

As shown in Table 4, the rate of spontaneous transformation of β to α during dry storage at ambient conditions is too slow and the period is uncertainly (Table 5).

4. Conclusions

The transformation α to β modification of chlorothalonil is an endothermic process, as determined by DSC, giving an endothermic peak in the range 150–175 °C. The transforming temperature, 150.5 ± 0.1 °C, and the enthalpy of transformation, ΔH_t, $4.03 \pm 0.03\,\mathrm{kJ\,mol^{-1}}$ (significance level = 0.02) were determined. The activation energy, E_a, was calculated to be $6.5 \pm 0.9 \times 10^2\,\mathrm{kJ\,mol^{-1}}$ (95% confidence limits). The rate of transformation of α to β modification is fast, but the reverse very slow. Spontaneous transformations of β to α under ambient conditions were also observed and the periods are scattered. The X-ray powder diffraction (XRD) patterns of the two modifications were measured, and the three strongest lines ($2\theta/°$) and relative intensity (I/I_0)) of each modification are given, relatively, 25.52 (100), 14.38 (56), 27.95 (47); 26.58 (100), 14.33 (6), and 54.77 (3).

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