Thermochimica Acta, 141 (1989) 151–157
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EFFECT OF CHEMICAL ADSORPTION OF CALCIUM OXALATE MONOHYDRATE ON DTA BASELINE

LIU HUAQING

Department of Chemistry, Jiangxi Normal University, Nanchang (China)

(Received 2 May 1988)

ABSTRACT

The anomalous exothermic peak of calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) at about 90 °C was investigated using the principle of chemical adsorption. The anomalous peak is due to chemisorption at the surface of the sample. The activation energy of adsorption $E_{ad} = 36.25$ kJ mol^{-1} was calculated using the method of Kissinger.

INTRODUCTION

The effects of variations in experimental parameters on the shape of the DTA curve are numerous. Equipment variables and sample variables can affect the DTA curve [1–3]. The initial deviation of the DTA curve (the DTA baseline deviates significantly after heating for a short time) due to adsorption is a common phenomenon which affects both qualitative and quantitative analysis of the DTA curve. There is little information about this phenomenon in the literature. By comparing the DTA curve of a sample under normal pressure conditions with that of a sample in a vacuum, it can be seen that chemisorption of the sample exists, certainly during a programmed heating process. This paper reports that chemisorption causes an anomalous exothermic peak and results in the deviation of the DTA baseline.

EXPERIMENTAL

Methods

DTA was carried out using an LCT-1 thermobalance (manufactured by the Beijing Optical Instrument Factory) in static air and in a vacuum. Samples of about 10 mg were used and the heating rate was 15 °C min^{-1}. Al_2O_3 was employed as a reference material.

0040-6031/89/$03.50

Samples

Calcium oxalate monohydrate (A) is a "calibration standard" material for both DTA and TG. It was obtained from the Beijing Optical Instrument Factory. The sample was in the form of small granules.

Calcium oxalate monohydrate (B) is analysis grade reagent. It was obtained from Shanghai Chemical Reagent Co. The sample was in the form of very small granules.

Both samples were dried at 80 ° C for 2 h.

RESULTS AND DISCUSSION

The DTA curves of calcium oxalate monohydrate ((A) and (B)) are shown in Fig. 1(a). An anomalous exothermic peak can be seen in the DTA curve of calcium oxalate monohydrate (B) between ambient temperature and about 100 ° C. The rest of the DTA curve is the same as that of calcium oxalate monohydrate (A). The anomalous peak results in a large deviation of the DTA baseline of calcium oxalate monohydrate (B). The area of this peak in the DTA curve of calcium oxalate monohydrate (B) decreases significantly under vacuum conditions (see Fig. 1(b)). The anomalous exothermic peak may be related to gas adsorption.

The thermal decomposition of calcium oxalate monohydrate takes place as follows

$$CaC_2O_4 \cdot H_2O \xrightarrow{150\text{–}245\,^\circ C} CaC_2O_4 + H_2O \qquad (1)$$

$$CaC_2O_4 \xrightarrow{390\text{–}495\,^\circ C} CaCO_3 + CO \qquad (2)$$

$$CaCO_3 \xrightarrow{850\,^\circ C} CaO + CO_2 \qquad (3)$$

Therefore in the DTA curve of calcium oxalate monohydrate, two endothermic peaks (due to the dehydration of the sample and the thermal decomposition of $CaCO_3$) and one exothermic peak (caused by the oxidation of CO with O_2 in air) can be seen. Obviously, the exothermic peak which characterizes the thermal decomposition of the sample does not exist in the temperature range from ambient to about 100 ° C.

Investigation of the anomalous peak using the principle of chemical adsorption [4]

For every atom surrounded by other identical atoms in the interior of a solid, the mutual force of attraction is saturated. However, for an atom on the surface of a solid, the force is not saturated because the force of attraction between the interior atoms of the solid and the surface atom is

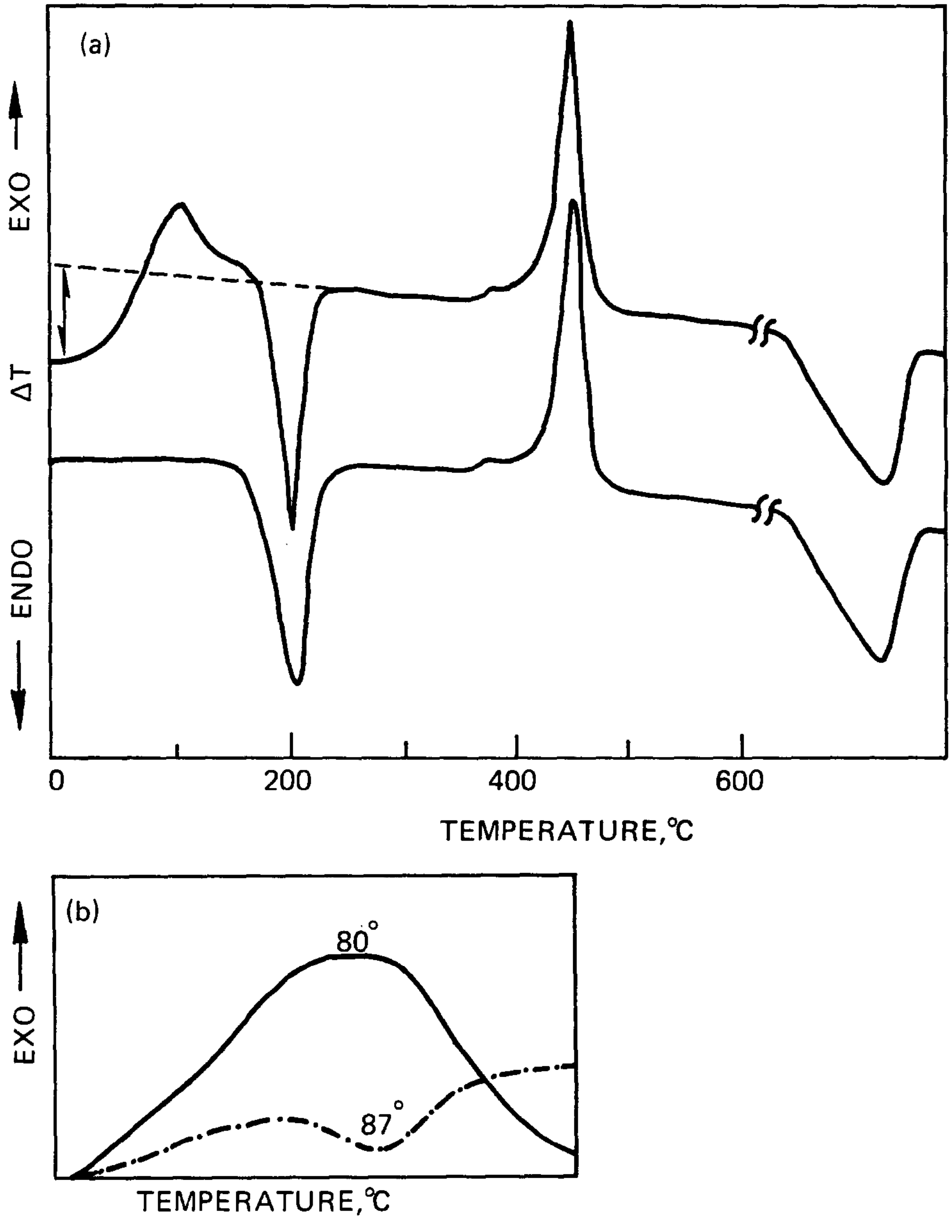

Fig. 1. (a) DTA curves of $CaC_2O_4 \cdot H_2O$ ((A) and (B)). (b) DTA curves of the anomalous exothermic peak of $CaC_2O_4 \cdot H_2O$ (B): ———, normal pressure; —·—·—, vacuum (10^{-3} mmHg).

greater than the force of attraction between the gas molecules and the surface atom. If an atom is moved from the interior of a solid to the surface energy must be expended. The extra energy of the solid (or liquid) surface is called surface energy. When gas molecules come into contact with the surface of a solid, the surface of the solid tends to reduce its surface energy by attracting the gas molecules using the van der Waals' force or the residual force between two atoms. The phenomenon is called adsorption. If the adsorbed molecules react chemically with the surface, the phenomenon is called chemisorption. Chemisorption is similar to a chemical reaction. Initially, gas molecules form an adsorption bond, which is similar to a chemical bond; then they form surface compounds with the surface of the solid. Since chemical adsorption bonds are broken and formed in the process of chemisorption, this process produces adsorption heat which has the same range of values as a chemical reaction, i.e. from a few kilocalories to as high as 100 kcal [5]. The heat is given by the thermodynamic formula

$$\Delta G = \Delta H - T \Delta S \tag{4}$$

when $\Delta G < 0$, i.e. chemisorption takes place spontaneously, the state of movement of the gas molecules after adsorption is more restricted than before adsorption, so that $\Delta S < 0$. If $\Delta G < 0$ and $\Delta S < 0$, then ΔH is also negative. A negative ΔH value proves that chemisorption is an exothermic process, which results in an exothermic peak. Therefore the anomalous peak in the DTA curve of calcium oxalate monohydrate (B) can be explained as being due to chemisorption.

Calculation of the activation energy of chemisorption using the method of Kissinger [6]

According to the Arrhenius equation of the relationship between the rate constant k and temperature T, we have

$$\mathrm{d}a/\mathrm{d}T = (A/\beta) \exp(-E/RT)(1-a)^n \tag{5}$$

assuming that the maximum rate of a reaction is at the maximum peak temperature, so that

$$\mathrm{d}^2 a/\mathrm{d}T^2 = 0 \tag{6}$$

The maximum peak temperature T_m is substituted into the differential form of eqn. (5)

$$\beta/T_\mathrm{m}^2 = (AR/E)\, n(1-a)^{n-1} \exp(-E/RT_\mathrm{m}) \tag{7}$$

Converting eqn. (7) to natural logarithms, we obtain

$$(\ln \beta)/T_\mathrm{m}^2 = \ln\left[(AR/E)\, n(1-a)^{n-1}\right] - E/R\, 1/T_\mathrm{m} \tag{8}$$

It is apparent that the plot of $(\ln \beta)/T_\mathrm{m}^2$ vs. $1/T_\mathrm{m}$ will yield the activation energy from the slope of the line. Some T_m values of the chemisorption peak of calcium oxalate monohydrate (B) at various heating rates are listed in Table 1. Figure 2 shows a plot of $(\ln \beta)/T_\mathrm{m}^2$ vs. $1/T_\mathrm{m}$ for chemisorption of the sample. The slope of the straight line in Fig. 2 is $k' = 4.36 \times 10^3$;

TABLE 1

Some T_m values of chemisorption of $CaC_2O_4 \cdot H_2O$ (B) at various heating rates β

β (°C min^{-1})	T_m (K)	$1/T_m \times 10^{-3}$	$(\ln \beta)/T_m^2$
5	336	2.976	−10.025
10	353	2.833	−9.430
15	363	2.755	−9.081
20	370	2.730	−8.831

TABLE 2

Some T_m values of dehydration of $CaC_2O_4 \cdot H_2O$ (B) at various heating rates β

β (°C min^{-1})	T_m (K)	$1/T_m \times 10^{-3}$	$(\ln \beta)/T_m^2$
5	457	2.188	−10.640
10	469	2.132	−10.00
15	472	2.199	−9.606
20	480	2.083	−9.352

therefore, the activation energy of chemisorption for calcium oxalate monohydrate (B) is $E_{ad} = k'R = 4.36 \times 10^3 \times 8.314 = 36.25$ kJ mol^{-1}.

In order to examine the E_{ad} value, the dehydration peak of calcium oxalate monohydrate (B) in the same DTA curve is treated using the method of Kissinger (see Table 2 and Fig. 3). The activation energy of dehydration E_{dh} for calcium oxalate monohydrate (B) is 99.57 kJ mol^{-1}. By comparing this experimental value with the literature value (92.1 kJ mol^{-1}) it can be

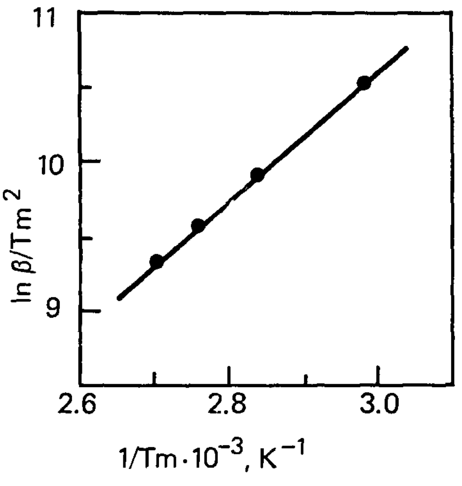

Fig. 2. Plot of $(\ln \beta)/T_m^2$ vs. $1/T_m$ for chemisorption of $CaC_2O_4 \cdot H_2O$ (B).

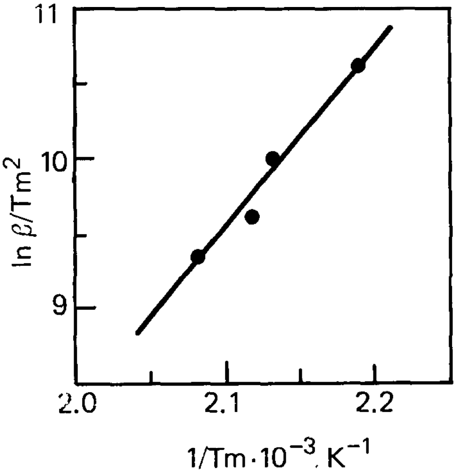

Fig. 3. Plot of (ln β)/T_m^2 vs. 1/T_m for dehydration of $CaC_2O_4 \cdot H_2O$ (B).

seen that the experimental error is in the range of the thermal analysis error. Therefore the values of both E_{ad} and E_{dh} are reliable.

CONCLUSIONS

The DTA baseline deviation caused by chemisorption differs from that caused by equipment variables and sample variables, because chemisorption is similar to a chemical reaction and results in a large change in the DTA curve. When chemisorption occurs on the surface of a solid sample in the temperature range from ambient to a slightly higher temperature, either an exothermic peak will be observed in the DTA curve or the DTA baseline will deflect towards the exothermic direction so that a new DTA baseline will be obtained after chemisorption is complete. This phenomenon is called the chemisorption effect on the DTA baseline. If we consider the factors which affect the DTA curve, other than sample variables and equipment variables, the chemisorption effect is the most noticeable, especially in the case of an initial large deviation of the DTA baseline.

ACKNOWLEDGEMENT

The author wishes to acknowledge the helpful comments and advice of Prof. Huang Fanzhu.

REFERENCES

1 M.I. Pope and M.D. Judd, Differential Thermal Analysis, Heyden, London, 1977, pp. 22–29.
2 W.W. Wendlandt, Thermal Methods of Analysis, Wiley-Interscience, New York, 1974.
3 C. Jinghwong, Thermal Analysis and its Application, Science Press, Beijing, 1985, pp. 232–257.
4 G.W. Castellan, Physical Chemistry, Addison–Wesley, Reading, MA, 1964, pp. 541–556.
5 G.W. Castellan, Physical Chemistry, Addison–Wesley, Reading, MA, 1964, p. 550.
6 H.E. Kissinger, J. Res. Nat. Bur. Stand., 57 (1965) 217.