

## **KINETIC ANALYSIS OF THE THERMAL DECOMPOSITION OF SYNTHETIC MALACHITE BY CRTA**

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### **Abstract**

The kinetic behavior of the thermal decomposition of synthetic malachite was investigated by means of CRTA under different conditions of reduced pressure, flowing gases and quasi-isobaric atmospheres. The thermal decomposition was found to proceed at lower temperatures under the influence of the self-generated gases, CO<sub>2</sub> and H<sub>2</sub>O. From a viewpoint of chemical equilibrium, the normal and opposite effects on the overall kinetics were observed for the self-generated CO<sub>2</sub> and H<sub>2</sub>O, respectively. The complexity of the present reaction is also reflected by the variations of the apparent kinetic parameters which depend on the applied and self-generated atmospheric conditions. The practical usefulness of CRTA when applied to a complicated thermal decomposition is discussed as exemplified by the kinetic approaches to the present reaction.

**Keywords:** CRTA, kinetics, self-generated atmospheric conditions, synthetic malachite, thermal decomposition

### **Introduction**

The kinetics of the thermal decomposition of synthetic malachite, Cu<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub>, have been studied by many workers [1–8]. A simple rate process has been assumed because the reaction is characterized by a smooth single-step TG trace to give copper(II) oxide: Cu<sub>2</sub>CO<sub>3</sub>(OH)<sub>2</sub> → 2CuO + CO<sub>2</sub> + H<sub>2</sub>O. Recently, Reading and Dollimore [9] reported the results of evolved gas analysis (EGA) during the thermal decomposition under controlled rate thermal analysis (CRTA). The two product gases, CO<sub>2</sub> and H<sub>2</sub>O, were not evolved at the same rate during the course of reaction. Interactions of the gaseous products with the solid product at the reaction interface were pointed out as a possible reason for this behavior. In our previous paper [10], this behavior was reconfirmed by EGA during linear heating in vacuum. Under reduced pressure conditions, it was confirmed by X-ray powder diffraction that the crystallization of solid product CuO is more or less impeded during the early stage of reaction. An interaction of the poorly crystallized CuO with evolved CO<sub>2</sub> seems to be responsible for the different evolution rates of CO<sub>2</sub> and H<sub>2</sub>O. It was also shown by conventional

non-isothermal TG [10] that the reaction temperature shifts to a higher temperature region with decreasing partial pressure of self-generated gases at the reaction sites caused by increasing the flow rate of dry  $N_2$  or by reducing the pressure. This behavior contrasts with the general trend of the thermal decomposition of solids, deduced from considerations based on chemical equilibrium. Because the increase of reaction temperature with increasing partial pressure of  $CO_2$  has been reported by Henmi *et al.* [11], it seems that the reaction is accelerated by the higher water vapor pressure generated by the reaction itself. Catalytic action of the water vapor on the crystallization of CuO seems to be attributed to the higher reactivity of the sample under higher partial pressures of evolved gases.

It is apparent from the results of previous papers [9, 10] that the kinetic characterization of the decomposition requires very complicated considerations concerning the chemical equilibrium of the reactant solid with the product gases, catalytic action of evolved water vapor on the crystallization of CuO, an interaction of evolved  $CO_2$  with poorly crystalline CuO and so on. Because the kinetic analysis of solid-state reactions by thermal analysis is a procedure for analyzing the kinetics at the reaction interface from the overall kinetic data, careful attention is required for controlling the influence of the self-generated atmospheric conditions on the overall kinetics during measurements. Compared with conventional isothermal and linear non-isothermal measurements, CRTA provides more reliable kinetic data for reactions where the influence of the self-generated atmospheric condition is significant, because the overall rate of evolution of product gases is very slow and remains constant during the course of reaction [12]. In the present study, the influence of the self-generated atmospheric conditions on the overall kinetics of the thermal decomposition of synthetic malachite is reinvestigated by means of CRTA under various atmospheric conditions. The practical usefulness of CRTA when applied to a complicated thermal decomposition is discussed as exemplified by the kinetic analysis of the present reaction.

## Experimental

### *Material*

Synthetic malachite was prepared by titration of 1.0 M  $CuSO_4$  solution with 1.0 M  $K_2CO_3$  solution [7]. The precipitate produced during the titration was aged, with mechanical stirring, in the mother liquor at 323 K for 2 h. The precipitate was filtered, washed with water and ethanol, and dried in air at 373 K. The product was identified by chemical analysis for  $Cu^{2+}$ , FTIR spectroscopy (Shimadzu FTIR8100), X-ray powder diffractometry (XRD: Rigaku RINT2200 with a Cu target and a monochromator), and TG-DTA (ULVAC TGD9600).

### *Instruments and measurements*

Two instruments were used for CRTA. The CRTA measurements under reduced pressure were performed using an instrument of the Rouquerol type [12], constructed

using a thermobalance (Cahn2000) and a vacuum pumping system. The residual pressure during the measurements under dynamic vacuum at a constant pumping rate was monitored and the decomposition rate was controlled by regulating the sample temperature so as to maintain the residual pressure constant during the decomposition. The sample was weighed into a hemispherical quartz crucible of 10 mm in diameter. The residual pressure of the balance system was reduced to  $2.0 \cdot 10^{-3}$  Pa. Using different sample masses,  $m_0$ , ranging from 2 to 25 mg, some ten CRTA measurements were performed by setting a heating rate of  $10 \text{ K min}^{-1}$  and controlling residual pressure of  $4.0 \cdot 10^{-3}$  Pa.

For measuring the CRTA curves under flowing gases, a commercial TG instrument (Shimadzu TGA-50) was remodeled to enable CRTA measurements to be made by monitoring the DTG signal. The sample was weighed into a platinum crucible of 6 mm in diameter and 4 mm in height. Under flowing dry  $\text{N}_2$  at a rate of  $50 \text{ ml min}^{-1}$ , the CRTA measurements, with  $m_0$  ranging from 5 to 35 mg, were carried out at a heating rate of  $10 \text{ K min}^{-1}$  and controlling rate of  $1.5 \cdot 10^{-2} \text{ mg min}^{-1}$ . The measurements under flowing wet  $\text{N}_2$  and mixed gases of dry  $\text{N}_2$  and  $\text{CO}_2$  were also performed under conditions similar to those under flowing dry  $\text{N}_2$ .  $\text{N}_2$  bubbled through water at 300 K and dry  $\text{CO}_2$ , respectively, were flowed at a rate of  $40 \text{ ml min}^{-1}$ , in addition to a dry  $\text{N}_2$  flow at a rate of  $10 \text{ ml min}^{-1}$  for purging the balance system. For measuring the CRTA curves under quasi-isobaric conditions, the sample was weighed into an aluminum crucible and sealed with an aluminum cap with an orifice of  $100 \mu\text{m}$  in diameter. The sealed samples, with  $m_0$  ranging from 5 to 25 mg, were subjected to CRTA measurements under flowing dry  $\text{N}_2$  at a rate of  $50 \text{ ml min}^{-1}$ .

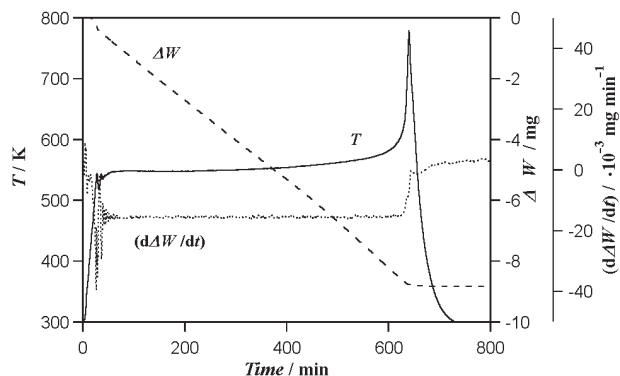
CRTA measurements with a cyclic rate-jump were also performed under reduced pressure and in flowing gases by means of the above instruments, respectively. For the measurements under reduced pressure, the controlling residual pressure was switched periodically between  $4.0 \cdot 10^{-3}$  and  $8.0 \cdot 10^{-3}$  Pa. The controlling decomposition rate was switched periodically between  $1.0 \cdot 10^{-2}$  and  $2.5 \cdot 10^{-2} \text{ mg min}^{-1}$  for the measurements under flowing gases and quasi-isobaric conditions.

## Results and discussion

In the CRTA measurements under reduced pressure, performed by setting the basal pressure at  $2.0 \cdot 10^{-3}$  and the controlling residual pressure at  $4.0 \cdot 10^{-3}$  Pa, the decomposition proceeded at a constant rate of  $1.5 \cdot 10^{-2} \text{ mg min}^{-1}$ . Accordingly, the CRTA measurements for the reaction under flowing gases were carried out by setting the controlling rate of mass loss to be  $1.5 \cdot 10^{-2} \text{ mg min}^{-1}$ . Figure 1 shows a typical CRTA record for the reaction under flowing dry  $\text{N}_2$  at a rate of  $50 \text{ ml min}^{-1}$ .

In the CRTA measurements, the following relationship exists between the controlled rate of mass loss,  $C$ , and the generalized reaction rate,  $d\alpha/dt$ .

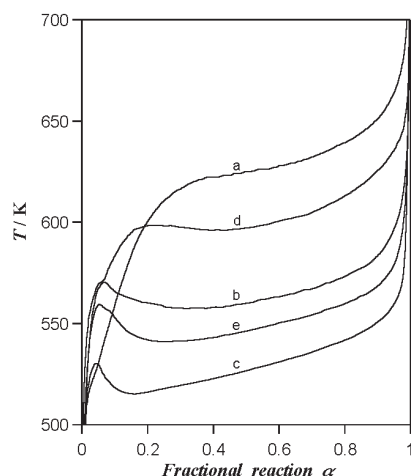
$$\frac{d\alpha}{dt} = \frac{C}{m_0 \Delta m} \quad (1)$$



**Fig. 1** Typical CRTA record for the thermal decomposition of synthetic malachite under flowing dry  $N_2$  at a rate of  $50 \text{ ml min}^{-1}$ . Sample mass  $m_0=30.82 \text{ mg}$

where  $\alpha$  and  $\Delta m$  are the fractional reaction and fractional value of total mass loss during the decomposition, respectively. When comparing the influence of the atmospheric condition on the temperature profile of the CRTA, the values of  $C$  and  $m_0$  have to be fixed among the measurements under different atmospheric conditions. Figure 2 compares the temperature profile of the CRTA measured at  $C=1.5 \cdot 10^{-2} \text{ mg min}^{-1}$  and  $m_0=15.0 \pm 0.2 \text{ mg}$  under different atmospheric conditions. Under vacuum, the reaction initiates at a lower temperature than in flowing dry  $N_2$  and quasi-isobaric atmospheres, followed by a continuous increase of the temperature as reaction proceeds, until around  $\alpha=0.3$ . At around  $\alpha=0.1$ , the reaction temperature exceeds that in flowing dry  $N_2$  and is higher by more than 50 K during  $\alpha>0.3$ . This tendency is in good agreement with the previously reported result of conventional non-isothermal analysis [10], where the reaction temperature increases when the influence of the self-generated gases is decreased by increasing the flow rate of  $N_2$ , or by reducing the pressure. For the reaction under flowing  $N_2$  at a rate of  $50 \text{ ml min}^{-1}$ , the temperature profile had a concave shape within the range  $\alpha>0.1$  with the minimum at  $\alpha=0.29$ . The concave shape of the temperature profile in CRTA indicates apparent kinetic agreement to a nucleation and growth type reaction [13]. This is also in agreement with the apparent rate behavior of the non-isothermal decomposition reported earlier [8–10]. Under the quasi-isobaric condition of the self-generated gases, the reaction temperature is lower than that in flowing dry  $N_2$ . The above results indicate that the unusual reaction behavior, characterized by the increase of the reaction temperature associated with the decrease in the influence of the self-generated gases, is observed in a wide range of applied reaction atmospheres, from the quasi-isobaric condition of ambient pressure to a reduced pressure of  $\sim 10^{-3} \text{ Pa}$ .

By comparing the CRTA curves recorded under different flowing gases (Fig. 2 (b), (d) and (e)), it is seen that the reaction temperature rises and falls by the effect of the atmospheric  $CO_2$  and  $H_2O$ , respectively. Because the evolution rates of  $CO_2$  and  $H_2O$  by the reaction itself have been maintained constant among the measurements under different gaseous atmospheres, the change in the reaction temperature with atmospheric gases indicates that, from the viewpoint of chemical equilibrium, the nor-



**Fig. 2** Temperature profiles of the controlled rate thermal decomposition of synthetic malachite under various atmospheric conditions. Sample mass  $m_0=15.0\pm 0.2$  mg and controlled rate  $C=1.5\cdot 10^{-2}$  mg  $\text{min}^{-1}$ ; a –  $4.0\cdot 10^{-3}$  Pa, b – flowing dry  $\text{N}_2$ , c – quasi-isobaric, d – flowing  $\text{N}_2\text{-CO}_2$ , e – flowing  $\text{N}_2\text{-H}_2\text{O}$

mal and opposite behaviors of the overall kinetics result from the influences of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , respectively. This characteristic behavior of the present reaction, which has been deduced in our previous paper [10], was verified in the present study as experimental evidence.

For analyzing the influence of the self-generated atmosphere on the reaction kinetics by CRTA, a series of CRTA curves with a fixed  $C$  and different  $m_0$  at an applied atmosphere was subjected to the kinetic calculation by assuming the following kinetic equation:

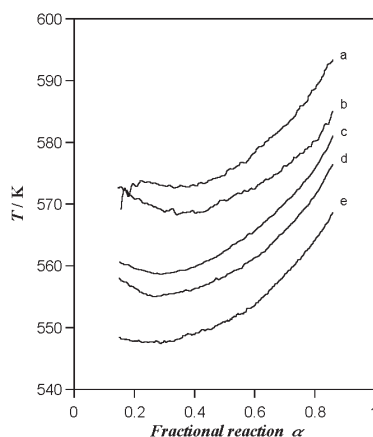
$$\frac{C}{m_0 \Delta m} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (2)$$

where  $f(\alpha)$  is the kinetic model function listed elsewhere [14–17]. The other symbols have the standardized meanings of the Arrhenius equation. From Eqs (1) and (2), we obtain

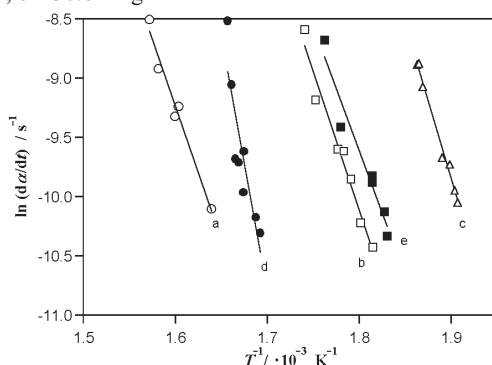
$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \quad (3)$$

Equation (3) indicates that the conventional Friedman method [18] can be applied to a series of CRTA curves with different  $m_0$  to obtaining the apparent value of  $E$  at a restricted  $\alpha$ .

Figure 3 shows typical CRTA curves recorded using different  $m_0$  under flowing dry  $\text{N}_2$ . The CRTA curves shift towards the higher temperature with decreasing  $m_0$ , as is expected from Eq. (2). Typical Friedman plots at  $\alpha=0.5$  were shown in Fig. 4. Within the range of  $0.2 \leq \alpha \leq 0.8$  in the respective series of kinetic data under different



**Fig. 3** Influence of sample mass on the temperature profiles of the controlled rate thermal decomposition of synthetic malachite under flowing dry  $N_2$  at a rate of  $50 \text{ ml min}^{-1}$ . Controlled rate  $C=1.5 \cdot 10^{-2} \text{ mg min}^{-1}$ ; a – 5.41, b – 8.35, c – 15.40, d – 21.23, e – 30.82 mg



**Fig. 4** Typical Friedman plots for the controlled rate thermal decomposition of synthetic malachite at  $\alpha=0.5$  under various atmospheric conditions; a –  $4.0 \cdot 10^{-3} \text{ Pa}$ , b – flowing dry  $N_2$ , c – quasi-isobaric, d – flowing  $N_2\text{-CO}_2$ , e – flowing  $N_2\text{-H}_2\text{O}$

conditions, the correlation coefficient  $\gamma$  of the linear regression analysis of the Friedman plot is better than  $-0.98$  and the variation of the slope is less than 10%. The values of  $E$  averaged over  $0.2 \leq \alpha \leq 0.8$  were listed in Table 1. The apparent values of  $E$  for the reactions in vacuum and in flowing dry  $N_2$  are in good agreement with those reported for the non-isothermal decomposition in flowing  $N_2$  [9, 10]. The value of  $E$  obtained for the reaction under quasi-isobaric condition is apparently larger than those values of  $E$ . An  $E$  value of about  $130 \text{ kJ mol}^{-1}$  has also been reported for the isothermal decomposition in flowing  $N_2$  [7] and for the non-isothermal decomposition under reduced pressure of  $1.5 \text{ Pa}$  and under static air [8, 10]. Because the overall rates of evolution of product gases and the self-generated atmospheric condition at the reaction interface are largely different among the conventional and CRTA measurements,

a more systematic investigation may be required to discuss the significance of the apparent agreement of the  $E$  values.

**Table 1** The apparent kinetic parameters calculated from the CRTA and cyclic CRTA curves of the thermal decomposition of synthetic malachite under various atmospheric conditions

| Atmosphere         | Friedman method    |              | Rate-jump method   |              | $m^4$ | $A/s^{-1}$           | $\gamma^5$ |
|--------------------|--------------------|--------------|--------------------|--------------|-------|----------------------|------------|
|                    | $E^1/kJ\ mol^{-1}$ | $\sigma_1^2$ | $E^1/kJ\ mol^{-1}$ | $\sigma_1^3$ |       |                      |            |
| Vacuum             | 190.8              | 7.0          | 193.7              | 12.5         | 0.9   | $6.54 \cdot 10^{12}$ | 0.9906     |
| Flowing $N_2$      | 192.1              | 6.5          | 222.4              | 13.8         | 1.4   | $9.65 \cdot 10^{13}$ | 0.9966     |
| Quasi-isobaric     | 223.8              | 6.7          | 226.0              | 19.6         | 0.7   | $7.69 \cdot 10^{17}$ | 0.9992     |
| Flowing $N_2-CO_2$ | 335.0              | 29.0         | 314.9              | 30.1         | 1.7   | $4.27 \cdot 10^{25}$ | 0.9803     |
| Flowing $N_2-H_2O$ | 166.8              | 9.4          | 155.3              | 14.5         | 1.5   | $6.63 \cdot 10^{11}$ | 0.9920     |

<sup>1</sup>averaged over  $0.2 \leq \alpha \leq 0.8$

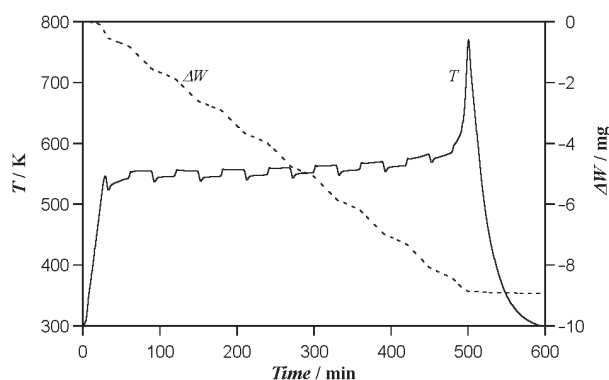
<sup>2</sup>averaged value of the standard deviation of the  $E$  values at various  $\alpha$

<sup>3</sup>standard deviation of the  $E$  values at various  $\alpha$

<sup>4</sup> $m(1-\alpha)[- \ln(1-\alpha)]^{1-1/m}$

<sup>5</sup>correlation coefficient of the linear regression analysis for the plot of  $d\alpha/d\theta$  vs.  $f(\alpha)$

Within the present results obtained by CRTA at a constant decomposition rate of  $1.5 \cdot 10^{-2} \text{ mg min}^{-1}$ , the apparent values of  $E$  tend to increase slightly with the increase in the influence of the self-generated gases, that is in the order of reduced pressure, flowing dry  $N_2$  and quasi-isobaric conditions. Comparing the  $E$  values obtained under different flowing gases, the value of  $E$  increases and decreases by the effects of atmospheric  $CO_2$  and  $H_2O$ , respectively. Deducing from the influences of atmospheric  $CO_2$  and  $H_2O$ , the change in the overall kinetics, observed among the reactions under reduced pressure, flowing dry  $N_2$  and quasi-isobaric condition, is likely to result from combined effects of self-generated  $CO_2$  and  $H_2O$ .



**Fig. 5** Typical cyclic CRTA record for the thermal decomposition of synthetic malachite under flowing dry  $N_2$  at a rate of  $50 \text{ ml min}^{-1}$ . Sample mass  $m_0=31.25 \text{ mg}$

For comparison, the apparent value of  $E$  was also determined from cyclic CRTA measurements using the rate-jump method [19]. Figure 5 shows the typical cyclic CRTA records with periodic rate-jump under flowing dry  $N_2$ . Because the values of  $\alpha$  before and after the rate-jump between  $C_1$  and  $C_2$  are assumed to be approximately constant, the value of  $E$  is calculated by the following equation:

$$E = -\frac{RT_1T_2}{T_2 - T_1} \ln \frac{C_1}{C_2} \quad (4)$$

The mean value of  $E$  determined by the rate-jump method within the range  $0.2 \leq \alpha \leq 0.8$  was also listed in Table 1. By comparing the  $E$  values determined by the Friedman method and the rate-jump method, close agreement can be found for the reaction other than those under flowing dry  $N_2$ . Under flowing dry  $N_2$ , the  $E$  value determined by the rate-jump method is larger by more than 10% than that determined by the Friedman method.

It is worth considering the methodological characteristics of the Friedman method and the rate-jump method. The evaluation of  $E$  by the Friedman method requires a series of kinetic curves at different reaction rates. In CRTA, the reaction rate can be altered by changing the controlling rate of mass loss,  $C$ , and/or the sample mass,  $m_0$ . Because the overall rate of evolution of product gases varies when the controlling rate of mass loss changes, the application to a reaction, which is influenced largely by the self-generated atmosphere, is not recommended. In the present study, the reaction rate was altered by changing the sample mass,  $m_0$ , and keeping the controlling rate of mass loss,  $C$ , constant, in order to maintain the overall rate of evolution of product gases constant. Careful attention is also required to the change in the influence of mass transfer phenomena among measurements with different values of  $m_0$  [20]. Changes in the overall rate of evolution of product gases and in mass transfer phenomena will affect the self-generated atmospheric condition, which is influenced also by the applied atmospheric condition.

A fairly large amount of sample has been used conventionally in the measurements of cyclic CRTA. In using a large amount of sample, a distribution of the fractional conversion among the respective sample particles in the reactant matrix probably exists during the course of reaction [21]. However, Reading *et al.* [19] reported for the thermal decomposition of calcium carbonate that the value of  $E$  determined by the rate-jump method is nearly constant over the wide range of sample mass used for the measurements. The rate-jump method is classified as an isoconversional method because of the approximation of constant  $\alpha$  before and after the rate-jump. The distribution of fractional conversion among the sample particles is also nearly identical before and after the rate-jump and is cancelled in evaluating  $E$  by an isoconversional method [21, 22]. This is one of the merits of the rate-jump method by cyclic CRTA. At the same time, the overall rates of evolution of product gases before and after the rate-jump are different in cyclic CRTA. It is noted, however, that application of the rate-jump method is based on the assumption that the influence of the change in the evolution rate on the kinetics is ignored [23].



By considering the characteristics of the methods of kinetic calculation applied to the CRTA and cyclic CRTA measurements, the agreement of the  $E$  values evaluated by the Friedman method and the rate-jump method, observed for the reaction other than those under flowing dry  $N_2$ , suggests that any changes of mass transfer phenomena in the series of CRTA with different  $m_0$ , and of the overall rate of evolution of product gases in the cyclic CRTA, can be ignored within the measuring conditions applied. On the other hand, the disagreement in the value of  $E$  for the reaction under flowing dry  $N_2$  can be explained by the influence of changes in mass transfer phenomena and/or in the overall rate of evolution of product gases on the decomposition kinetics.

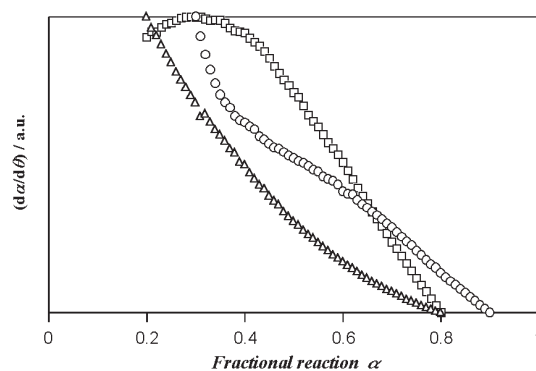
According to the following equation [24–26], the experimental master plots of  $d\alpha/d\theta$  vs.  $\alpha$  for the reaction under different atmospheric conditions, were drawn by extrapolating the rate data to infinite temperature using the value of  $E$  determined by the Friedman method:

$$\frac{d\alpha}{d\theta} = \frac{d\alpha}{dt} \exp\left(\frac{E}{RT}\right) = Af(\alpha) \quad (5)$$

where  $\theta$  is the generalized time proposed by Ozawa [27] and expressed by:

$$\theta = \int_0^t \exp\left(-\frac{E}{RT}\right) dt \quad (6)$$

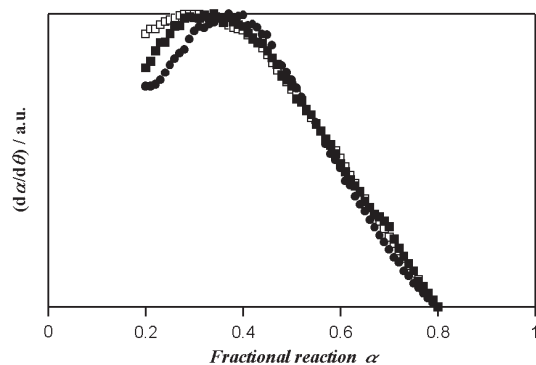
Figure 6 compares the experimental master plots for the reaction under reduced pressure, flowing dry  $N_2$  and quasi-isobaric conditions. The shape of the master plots varies remarkably with the influence of the self-generated gases. By comparing the experimental master plots for the reactions under vacuum and under flowing dry  $N_2$ , apparently different rate behavior is observed in the range of  $\alpha < 0.4$  and subsequently the value of  $d\alpha/d\theta$  decreases linearly as reaction proceeds under both conditions. Similar behavior in the latter half of the reaction has been reported for the non-iso-



**Fig. 6** Experimental master plots of  $d\alpha/d\theta$  vs.  $\alpha$  for the controlled rate thermal decomposition of synthetic malachite under reduced pressure, flowing dry  $N_2$  ( $\square$ ) and quasi-isobaric ( $\Delta$ ) conditions, ( $\circ$ )  $-4.0 \cdot 10^{-3}$  Pa

thermal decomposition under a reduced pressure of 1.5 Pa and in static air [10]. The variation of the rate behavior in the range of  $\alpha < 0.4$  with the temperature and atmospheric conditions applied indicates that the influence of the self-generated atmospheric condition on the kinetics is significant during the first half of the reaction. The concave shape of the experimental master plot observed for the reaction under quasi-isobaric condition shows that the overall rate behavior is regulated by a rate law of a diffusion-controlled reaction [28]. The reaction seems to proceed under quasi-equilibrium condition between the reactant solid and product gases and the removal of the product gases through the pinhole of the sample pan regulates the reaction rate.

Figure 7 compares the experimental master plots for the reaction under different flowing gases. Although the reaction temperature and the apparent value of  $E$  were influenced largely by the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the flowing gases, the experimental master plots show a similar shape with a maximum at around  $\alpha = 0.3$ . The change in the shape is again observed during  $\alpha < 0.3$ .



**Fig. 7** Experimental master plots of  $d\alpha/d\theta$  vs.  $\alpha$  for the controlled rate thermal decomposition of synthetic malachite under flowing various gases; (□) flowing dry  $\text{N}_2$ , (●) flowing  $\text{N}_2\text{-CO}_2$ , (■) flowing  $\text{N}_2\text{-H}_2\text{O}$

According to Eq. (5), the empirical best fitting of the experimental master plots to an appropriate  $f(\alpha)$  was examined by plotting  $d\alpha/d\theta$  vs. various  $f(\alpha)$ . The most appropriate conversion function  $f(\alpha)$ , giving the best linear fits for the reactions under the various atmospheric conditions, are listed in Table 1, together with the apparent values of  $A$  obtained from the slopes of  $d\alpha/d\theta$  vs.  $f(\alpha)$  plots. Irrespective of the atmospheric conditions applied, the experimental master plots of the present reaction fitted the Avrami–Erofeev type function. The kinetic exponent,  $m$ , in the Avrami–Erofeev function and the apparent value of  $A$  varied with the atmospheric condition applied. The concave shape of the experimental master plots for the reactions under vacuum and quasi-isobaric conditions was reflected by the values of  $m < 1$ . The experimental master plots, with a maximum at around  $\alpha = 0.3$ , for the reactions under flowing gases were characterized by the kinetic exponent  $1 < m < 2$ . The variation of the  $A$  value is associated with the change in the  $E$  value, indicating an apparent kinetic compensation effect [23]. The variation of the apparent kinetic parameters with the applied and

self-generated atmospheric conditions indicates that a quantitative understanding of the influence of CO<sub>2</sub> and H<sub>2</sub>O on the reaction kinetics is required to discuss the physico-chemical meanings of the apparent kinetic parameters for the present reaction.

## Conclusions

It was reconfirmed, by CRTA under various atmospheric conditions, that the decomposition temperature of synthetic malachite is considerably influenced by the self-generated atmospheres. CRTA provided experimental evidence that, from the viewpoint of chemical equilibrium, the self-generated CO<sub>2</sub> and H<sub>2</sub>O have normal and opposite effects on the overall kinetics, respectively. The apparent kinetic parameters also varied with the applied and self-generated atmospheric conditions. Although a more quantitative control of the self-generated atmospheric condition during measurements is needed for characterizing the kinetics of the present thermal decomposition, the trend of the effects of the self-generated gases on the overall kinetics was clearly represented by CRTA.

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