



RCTA TECHNIQUES USED IN STUDIES OF SOLID STATE REACTIONS IN INORGANIC COMPOUNDS*

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Abstract

The Reaction Controlled Thermal Analysis techniques, RCTA, are very useful both in thermogravimetric and dilatometric studies. In the present paper this big family of techniques is divided into three main classes: Quasi-Isothermal techniques (QIA); Controlled Reaction Rate Thermal Analysis (CRTA) and Reaction (Event) Controlled Heating Rate Adaption. After a short presentation of these techniques and the general advantages of RCTA, two examples of kinetic studies on thermal decomposition of Ba- and Ce oxalates by using Stepwise Isothermal Analysis, SIA, introduced by the author is presented and discussed.

Keywords: kinetics, reaction controlled thermal analysis, stepwise isothermal analysis, thermogravimetry

Introduction

Since the introduction of thermal analysis more than forty years ago, most studies of solid state reactions have been performed by using standard constant heating rate techniques. Although advanced computerised techniques are now available, these non-isothermal techniques still suffer from several inherent disadvantages such as a lack of separation of close-lying reactions, sensitivity towards crucible shape and thermal effects, which all restrict the accuracy that can be obtained by these techniques.

However new high resolution techniques have been introduced in several commercial equipment recently. These techniques, which are essentially based on the 'reaction rate controlled' thermal analysis techniques introduced by Paulik and Paulik [1], Rouquerol [2] and Sørensen [3] in the seventies, have proved to be very useful both in thermogravimetric and dilatometric studies.

One of the advantages of the stepwise isothermal analysis, SIA, introduced by Sørensen [3] is that the reactions can be studied under strictly isothermal conditions.

* Invited lecture.

Therefore this technique is especially suitable for kinetic studies and as an example of such studies, the results obtained in a recent work on the kinetics of the thermal decomposition of barium oxalate hemihydrate [4] will also be discussed in this paper

Reaction controlled thermal analysis

The techniques used in 'reaction controlled thermal analysis' are generally what can be called as 'event-controlled techniques', i.e. when an event such as a thermal decomposition, an evaporation or oxidation or shrinkage during sintering (dilatometry) takes place in the sample during the continuous heating as performed in conventional thermal analysis, then a change in the mode controlling the measuring condition is 'triggered'. These techniques should therefore be called as 'reaction controlled thermal analysis', which could appropriately be abbreviated as RCTA, rather than 'controlled rate thermal analysis', CRTA, as proposed by Rouquerol [2].

Generally there are several parameters which can be used to control the measuring conditions in RCTA. As illustrated in Fig. 1 they, for instance, can be the mass (thermogravimetry), the physical dimensions (dilatometry) or the gases evolved during a decomposition (evolved gas analysis). The principle involved in these techniques, irrespective of the controlling parameter, is generally as follows: when the sample reaches a transformation temperature, the resulting change in the controlling parameter, mass, length, gas pressure or concentration of a specific gas – will trigger a change in the measuring conditions, which will be maintained during the transformation. In the case of the Stepwise Isothermal Analysis technique introduced by Sørensen [3], for instance, the controlling parameter is the transformation rate,

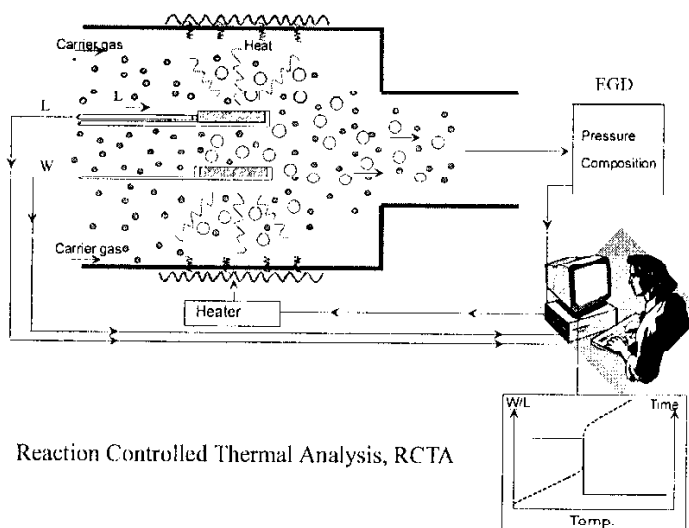


Fig. 1 Parameters generally used in controlling the measuring conditions in RCTA techniques

which is calculated for each data point by the computer. At the transformation temperature, where a change in the transformation rate takes place, the heating will be stopped when this rate exceeds a preset threshold value and the heating will not be resumed until the rate is again below this threshold value. By this technique the mode controlling the measuring conditions is automatically changed from continuous heating to constant temperature, and the transformation will thus by this technique take place isothermally, which, for instance, is of great importance in kinetic studies.

Generally the techniques used in RCTA can be divided into three main groups according to the mode selected and the techniques used to control the measuring conditions. The characteristic features of these are:

Quasi isothermal – quasi isobaric analysis proposed already in 1971 by Paulik and Paulik [1,6]. In the Derivatograph developed by these authors [7], a small mass change caused the light signal of the DTG galvanometer to fall on the cell controlling the power input to the furnace. In this system the heating was therefore immediately switched off when a transformation was initiated in the sample. As this system was very sensitive, this switching on and off of the heating caused the temperature to raise only very slowly. The Pauliks therefore called this technique as quasi-isothermal.

Another important feature of this technique is that the quasi isothermal conditions could only be achieved by using a labyrinth crucible, from which the gases could only escape very slowly. In the case of thermal decompositions, the reactions therefore took place in 'self-generated' atmospheres, under equilibrium pressure and the Pauliks therefore also termed their technique as quasi-isobaric.

Finally it is worth noting that by using the combined effect of the mechanical design of the system and the use of labyrinth crucibles it was possible to perform studies of thermal decompositions at a constant, but not programmable, transformation rate, which, of course, had several advantages, such as a better separation of closely lying reactions.

In the second group of RCTA techniques, the controlled transformation rate thermal analysis, CRTA, it is also possible to perform analysis at constant, and in this case at programmable transformation rates. In these techniques, which actually was proposed by Rouquerol [8] already in 1964, the controlling parameter is the pressure or the composition of the gases evolved during the thermal decomposition (Fig. 1) and therefore these techniques are very sensitive. The change in the physical property being studied, for instance the mass, can by this technique be measured by using a predetermined programme, but generally these measurements are performed at constant reaction rate. Recently a very interesting CRTA technique was introduced by Criado *et al.* [9], the constant acceleration technique where the rate is linearly increased with time. This technique is particularly interesting in kinetic studies since it allows the determination of both the reaction mechanism and the activation energy in one experiment.

For the third group, which probably comprises the largest number of techniques, the reaction is allowed to run freely, but under controlled temperature conditions. These techniques could therefore be called as: reaction (event) controlled heating rate adaption techniques as proposed by Schenker and Riesen [5]. Generally these

techniques can be divided into four types according to the heating mode chosen for the reaction:

- Constant temperature – i.e. isothermal conditions, Stepwise Isothermal Analysis (SIA) [3];
- Constant, but reduced heating rate [5];
- Dynamic heating rate, where the heating rate is changed during the reaction [10,15];
- Modulated Thermogravimetric Analysis (MTGA) [15], where the sample is superimposed a sinusoidal temperature modulation during the reaction.

For these techniques the change in the heating mode is generally triggered when the reaction rate, dW/dt or dL/dt , reaches a preselected threshold value, as illustrated in Fig. 2, either during the continuous heating or after completion of the reaction. In the case of the SIA technique two threshold values are applied, one value, which is the highest, for detecting the onset of the reaction and a much smaller value at the end of the reaction. In this way, the 'tail' of the reaction which is often very long, is also taken into account, which considerably improves the resolution. This was demonstrated by the author in a study of the thermal decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in which it was shown, that the SIA technique controlled in this way is capable of separating the release of the two first water molecules, which generally takes place in overlapping reactions in the temperature range $65\text{--}110^\circ\text{C}$ if analyzed by conventional thermal analysis, into four steps at the temperatures $58, 68, 75$ and 85°C respectively. The SIA technique thus gives a very high resolution, but on the other hand, these analyses are also very time consuming. The other techniques in this group were therefore introduced to achieve a reasonable resolution with the shortest possible measuring time.

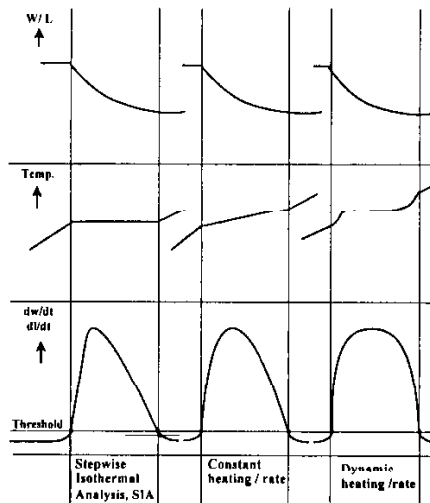


Fig. 2 Principles of temperature regulation in 'heating rate adaption' techniques

Finally, MTGA, introduced recently by TA Instruments [15] has proved to be a useful technique in kinetic studies, mainly in lifetime measurements on organic materials, but it has also been used in studies of thermal decompositions in inorganic compounds. In this technique a sinusoidal temperature modulation is superimposed on the underlying heating profile, which can be either constant temperature or dynamic heating during the reaction. The result is an oscillatory response in the rate of mass loss from which the kinetic parameters, i.e. the activation energy and the pre-exponential factor in the Arrhenius equation can be determined continuously by using discrete Fourier transformation (DFT) calculations. Compared to the method proposed by Flynn and Wall [16] for lifetime predictions of organic compounds (ASTM E 1640 [17]), which requires several measurements performed at different heating rates, MTGA allows determination of the parameters in a single experiment. As the activation energies are determined continuously during the decomposition process this technique is especially suitable for studies of autocatalytic reactions (n th -order reactions) in which the activation energy typically changes with the degree of conversion. Another advantage of this technique is that it is 'model free' as the kinetic function does not need to be known for the calculation. On the other hand, this technique is less suitable for determination of the mechanism controlling the reaction.

Compared to conventional non-isothermal techniques, the RCTA techniques have the following advantages:

1. Reactions takes place under near equilibrium conditions;
2. Improved resolution;
3. Quantitative calculations possible on each individual reaction;
4. Accurate reaction temperatures can be determined;
5. Suitable for kinetic studies;
6. In the case of SIA, the reactions takes place under 'strictly' isothermal conditions and this technique is thus specially suitable for kinetic studies;
7. In the case of MTGA the kinetic parameters can be determined continuously in a single experiment without prior knowledge of the reactions mechanism.

SIA used in kinetic studies

Kinetic analysis

For a thermal decomposition of the type



the kinetic equation can be expressed in the integral form as:

$$kt = g(\alpha) \quad (2)$$

or in the differential form as:

$$d\alpha/dt = kf(\alpha) \quad (3)$$

where α is the fraction reacted at the time t , $g(\alpha)$ and $f(\alpha)$ are functions of α depending on mechanism controlling the reaction, and k is the rate constant, which can be expressed by the Arrhenius equations as:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

where A is the pre-exponential factor (frequency factor) and E the activation energy.

In kinetic studies it is important to determine both the reaction mechanism as expressed by $f(\alpha)$ or $g(\alpha)$ as well as the two kinetic parameters, the pre-exponential factor and the activation energy.

As shown in the previous section, the advantage of SIA is that even close-lying reactions can be resolved and they take place under isothermal conditions. SIA is thus suitable for establishing the reaction mechanism. However, the main drawback of the SIA technique is that the kinetic parameters cannot generally be obtained as the reactions by this technique takes place in one isothermal step (Eq. 4).

Forced stepwise isothermal analysis

In order to overcome this problem the author introduced the forced stepwise isothermal analysis technique, FSIA [3], by which isothermal data can be obtained for a given reaction at different temperatures. In this technique the temperature is forced to increase in predetermined steps after a predetermined mass loss (thermogravimetry). An example of the mass loss curves obtained by using this technique in a study on the thermal decomposition of Ce-carbonate ($\text{Ce}_2\text{O}(\text{CO}_3)\text{H}_2\text{O}$) in different atmospheres [3,11], is shown in Fig. 3.

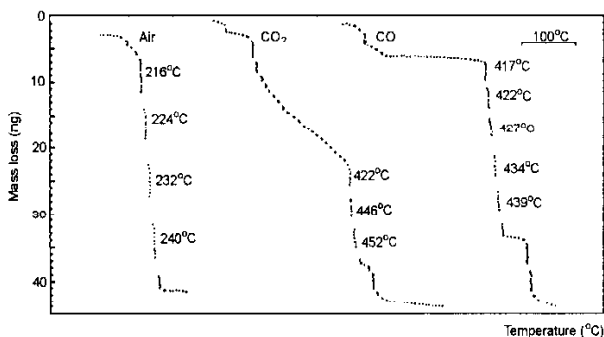


Fig. 3 Forced Stepwise Isothermal Analysis curves for decomposition of Ce-carbonate in different atmospheres

Plotting $g(\alpha)$ vs. t using the data in Fig. 3 gives the segments of straight lines with characteristic slopes as shown in Fig. 4 for the measurements in air and CO. The equations describing the mechanism controlling the thermal decompositions in these atmospheres are:

$$\text{in air: } F_{11} = g(\alpha) = \frac{1}{2}(-\ln(1 - \alpha))^2$$

which indicates that the controlling mechanism in this atmosphere is nucleation followed by two dimensional growth controlled by phase boundary movement;

$$\text{in CO: } F_7 = g(\alpha) = 2(1 - (1 - \alpha)^{1/2})$$

which indicate that in this atmosphere the mechanism is nuclei growth controlled by movement of phase boundaries.

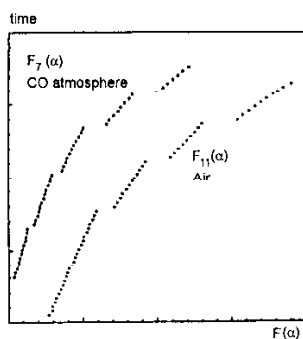


Fig. 4 $F(\alpha)$ vs. time plots for FSIA data determined from Fig. 3

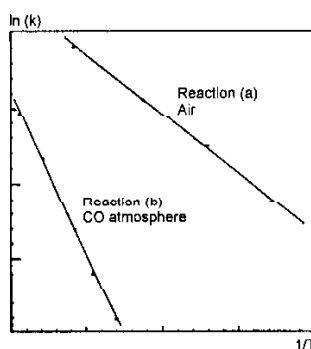


Fig. 5 Arrhenius plot obtained from the FSIA data given in Fig. 4

Finally plotting the Arrhenius constant k , which can be determined from the slopes of the segmented lines ($1/k$) shown in Fig. 4, as a function of the reciprocal temperature, $1/T$, straight lines obtained for the two atmospheres as shown in Fig. 5 is obtained. The activation energies calculated from the slope of these lines give 104.9 and 297.8 kJ mol^{-1} , respectively for the two atmospheres. The thermal decomposition thus takes much more easily place in air than in CO.

Combined SIA and non-isothermal thermogravimetry

Non-isothermal thermogravimetry with a linear temperature increase has been widely used as a tool for deriving kinetic parameters such as the activation energy and the pre-exponential factor in the Arrhenius equation in spite of the difficulty of separating close-lying reactions. Combining SIA and non-isothermal techniques, however, is a powerful tool for precise kinetic studies in which both the reactions mechanism and the kinetic parameters can be determined accurately.

It was demonstrated in a recent study [4] of thermal decomposition of barium oxalate hemihydrate $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$, which is an important starting material in synthesis of many double or multicomponent oxides [12]. The TG diagrams obtained for this compound using SIA and non-isothermal thermogravimetry are presented in Figs 6 and 7.

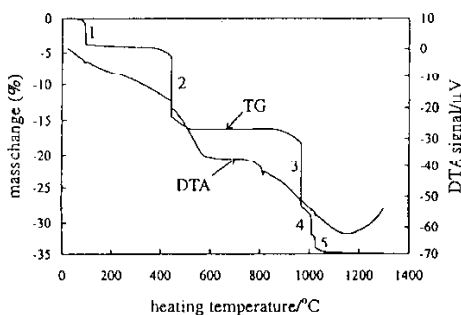


Fig. 6 SIA curves for decomposition of Ba-oxalate hemihydrate in air

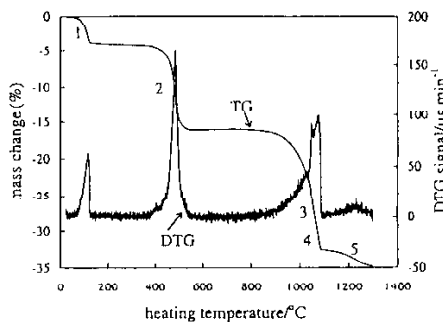


Fig. 7 Non-isothermal TG curves for decomposition of Ba-oxalate hemihydrate in air

Already from these diagrams it is clear that the SIA technique, besides providing isothermal data gives a much better resolution, especially for the high temperature thermal decomposition. Based on the SIA data presented in Fig. 6 we propose the following steps for the thermal decomposition of $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$:

1. $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O} \rightarrow \text{BaC}_2\text{O}_4 + 0.5\text{H}_2\text{O}$
2. $\text{BaC}_2\text{O}_4 \rightarrow \text{BaCO}_3 + \text{CO}$
3. $3\text{BaCO}_3 \rightarrow \text{BaCO}_3 \cdot (\text{BaO})_2 + 2\text{CO}_2$
4. $\text{BaCO}_3 \cdot (\text{BaO})_2 \rightarrow (\text{BaCO}_3)_{0.5} \cdot (\text{BaO})_{2.5} + 0.5\text{CO}_2$
5. $(\text{BaCO}_3)_{0.5} \cdot (\text{BaO})_{2.5} \rightarrow 3\text{BaO} + 0.5\text{CO}_2$

SIA thus reveal that intermediate basic carbonates of the type $\text{BaCO}_3 \cdot \text{BaO}$ are formed by thermal decomposition in the solid phase at high temperatures. This is in accordance with results published by Baker [13].

In order to determine the mechanism of the controlling reaction the SIA data were fitted to Eqs (2) and (3) by the linear least-squares method using different forms of $g(\alpha)$ and $f(\alpha)$. The controlling mechanism was selected by this method as the mechanism giving the best fit, i.e. the highest correlation coefficient, both by the integral and the differential method. The controlling mechanism which was the same for the five decompositions was found to be a two dimensional (cylindrical symmetry) phase boundary controlled process, which can be expressed by the Avrami-Erofeev equations:

$$f(\alpha) = (1 - \alpha)^{1/2}; \quad g(\alpha) = 2[1 - (1 - \alpha)^{1/2}]$$

Knowing the controlling mechanism, now it is easy to determine the kinetic parameters from the non-isothermal data (Fig. 7) by using the Coats and Redfern equation [14]:

$$\ln[g(\alpha)/T^2] = \ln(AR/QE)[1 - 2RT/qE] - E/RT$$

where E is the activation energy, q is the heating rate ($q = dT/dt$) and the other terms have their usual meanings.

A similar equation can, of course, be devised by using the differential form of the basic kinetic equation (Eq. (3)).

Plotting $\ln[g(\alpha)/T^2]$ vs. $1/T$ a linear curve should therefore be obtained for the correct mechanism, from which the activation energy E can be determined from the slope and knowing this value the pre-exponential factor, A , can be calculated from the intercept. Using this technique the following activation energies and pre-exponential factors were determined for the five steps:

	kJ mol^{-1}	$\ln A/\text{s}^{-1}$
1.	87.0 ± 0.7	20.6 ± 0.2
2.	296.0 ± 14.6	40.3 ± 2.5
3.	298.2 ± 14.3	21.3 ± 2.3
4.	381.0 ± 11.3	41.7 ± 1.6
5.	332.1 ± 9.3	21.2 ± 1.2

The values presented here are the average of the values obtained using the differential and the integral form of the Coats-Redfern equation.

For a more detailed discussion of the activation energies, the original publication [14] should be consulted.

Conclusions

In summary, the reaction controlled thermal analysis techniques, RCTA, have proved to be very useful both in thermogravimetric and dilatometric studies. Generally these techniques can be divided into three main classes depending on the mode selected to control the measuring conditions: Quasi-Isothermal Analysis (QIA), Controlled Reaction Rate Thermal Analysis (CRTA) and Reaction (Event) Controlled Heating Rate Adaption.

One of the main advantages of these techniques compared to standard non-isothermal thermal analysis is the improved resolution of even close-lying reactions. Therefore these techniques are useful in quantitative and in kinetic studies and they have been introduced in commercial instruments as 'high resolution techniques'.

Due to the high resolution that can be obtained by these techniques they have been used extensively during the last 10–15 years in studies of solid state reactions in inorganic compounds. In these studies new and accurate data were generated both on reaction temperatures and on kinetic parameters such as controlling reaction mechanisms and activation energies, some of which were presented in this paper.

An especially promising technique for kinetic measurements recently introduced by TA Instruments is the Modulated TGA technique, MTGA. By this technique kinetic parameters such as activation energies and pre-exponential factors in the Arrhenius equation can be determined continuously during the measurements. Therefore MTGA is especially useful in studies of thermal decomposition of both inorganic and organic compounds.

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