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Analysis of non-isothermal reaction kinetics. Part 2. Complex reactions

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Abstract

The theoretical behavior of complex reactions as a function of heating rate is discussed. The complex reactions in this study include single-step reactions (competitive and multiple reactions) and sequential reactions. Depending on the reaction temperature range, the nature of the complex reaction has been found to be significantly different. The isokinetic temperature has been found to provide a useful reference point to study and understand the behavior of complex reactions. The use of the "pseudo" order of reaction approach has been found to have limited applications in predicting the behavior of complex reactions. For the sequential reaction scheme it has been found that it is easier to identify the sequential nature of the reaction if a low activation energy reaction is followed by a high activation energy reaction, when compared to the reaction sequence in which a high activation energy reaction is followed by a low activation energy reaction.

INTRODUCTION

The study of thermal decomposition reactions of condensed phase materials such as biomass, coal, oil shale and polymers, is hindered by both inherent complexity and associated physical phenomena. The decomposition reactions generally involve a set of many simultaneous single-step reactions and/or sequential reactions. Non-isothermal analysis can be very useful in understanding the behavior of complex reactions [1–8]. Thermogravimetric (TG) methods provide limited information on the nature of complex reactions. Combination of TG with differential scanning calorimetry (DSC) or combined TG analysis techniques such as TG–MS, TG–IR or TG–FTIR provide a valuable tool with which to study the mechanism of complex reactions. Agrawal [1] has shown that if the reaction rate is not

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Dedicated to Professor Joseph H. Flynn in honour of his 70th birthday

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proportional to the sum of the amounts of the individual species, then DSC and TG will not yield identical results, thus helping to identify the presence of a complex reaction. The combination of TG with an additional analysis system is not always available and is expensive. By using the multiple heating-rate technique, TG data can be used to provide useful information on the nature of complex reactions [2,3]. Because TG devices are more widely available, this paper explores the use of data generated from simulated TG devices by the multiple heating-rate technique to aid in the identification and understanding of the complex nature of a reaction.

BRIEF REVIEW

Ozawa [2] and Flynn [3] have analyzed the effect of heating rate on simultaneous single-step reactions (including both parallel competitive reactions and multiple independent reactions) and have shown that multiple reactions can be separated into individual reactions by varying the heating rate. The separation is possible for the individual reactions with large differences in activation energy. The separation of the individual reactions is possible because low activation energy reactions dominate the kinetics at low heating rates and low temperatures; and high activation energy reactions dominate the kinetics at fast heating rates and high temperatures. This indicates that differences in the reaction rate causes the separation of the individual reactions in the complex mixture. This implies that separation of reactions is not possible for those individual reactions whose activation energies are of the same order of magnitude.

Examining the nature of multiple reactions, Agrawal [4] concluded that no generalization regarding the behavior of overall multiple reactions can be made. This is because the nature of the overall multiple reaction is a function of the composition of the reaction mixture, the rates of individual reactions and the activation energy of individual reactions (E_i). However, the temperature range and the activation energy E of the overall multiple reaction is confined within those of the individual reactions.

For an overall competitive reaction, Agrawal [4] found that the overall E reflects the average of the E_i values of the individual reactions, if the individual rates are comparable. In such a case the rate constant can be represented satisfactorily by the Arrhenius equation. If the rates of individual reactions are significantly different, then the overall E reflects the value of E_i of the most dominating reaction or reactions. This results in a "non-Arrhenius" behavior of the overall rate constant. Non-Arrhenius behavior implies that a single set of Arrhenius parameters is insufficient to model the effect of temperature on the rate constant. The E value for the overall competitive reaction is limited by the maximal and minimal values of the individual activation energy.

In cases where reaction rates and E values are significantly different, the overall reaction may indicate the trend of a "pseudo" nth order reaction [4]. Some studies have been reported on modeling complex reactions by an nth order reaction. Modeling the overall reaction by an nth order reaction has limited applications because changes in the heating rate and/or the composition of the reaction mixture result not only in changes in the "pseudo" order of reaction but also in the Arrhenius parameters.

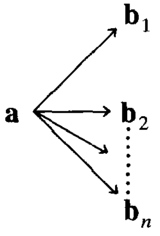
Some work has also been reported on modeling sequential reactions [5,6]. Heide et al. [5] have reported that an increase in the differential of the activation energy of individual reactions causes a better separation of the individual reactions. For the same differential in E_i, Heide et al. [5] have shown that at low values of the activation energy it is easier to separate the peaks than with high values of E. Separation of the individual reactions is also possible by varying the pre-exponential factor [5], which is equivalent to changing the heating rate.

KINETIC ANALYSIS

For the purpose of this discussion, complex reactions have been categorized into two kinds: (a) single-step reactions and (b) sequential or consecutive reactions. These reactions are discussed in the following sub-sections.

Single-step reactions

Parallel-competitive and multiple-independent reactions fall into the category of single-step reactions. Some theoretical research has been reported on the thermal behavior of complex single-step reactions by non-isothermal methods [1–4,7–9]. These reactions include, parallel-competitive reactions



and multiple independent reactions

$$\begin{array}{ccc} \mathbf{a}_1 & \longrightarrow & \mathbf{b}_1 \\ \mathbf{a}_2 & \longrightarrow & \mathbf{b}_2 \\ \vdots & & \vdots \\ \mathbf{a}_n & \longrightarrow & \mathbf{b}_n \end{array}$$

where **a** represents the reactants and **b** the products. Subscripts are used to identify the individual reactions. No subscript is used for the overall reaction. For the (overall) competitive reaction, the rate is given by the expression

$$\mathrm{d}a/\mathrm{d}T = -(a/\beta)\sum A_i \exp(-E_i/RT) \quad (1)$$

and

$$a = \prod a_i \quad (2)$$

For the multiple reaction case, the individual reaction rate is represented as

$$\mathrm{d}a_i/\mathrm{d}T = [a_i(A_i/\beta)] \exp(-E_i/RT) \quad (3)$$

and the (overall) multiple reaction rate is represented as

$$\mathrm{d}a/\mathrm{d}T = \sum g_i \, \mathrm{d}a_i/\mathrm{d}T \quad (4)$$

and

$$a = \sum g_i a_i \quad (5)$$

where g_i is the weight factor and $\Sigma g_i = 1$. The discussion in this paper is limited to first-order reactions. Further details on the kinetic expressions are available in the literature [3,4].

Table 1 summarizes the Arrhenius parameters for individual reactions chosen for this study in order to examine the behavior of single-step complex reactions by non-isothermal techniques. The order of reaction is assumed to be one. The isokinetic temperature (see Agrawal [10] for details on the isokinetic temperature), the temperature at which the reaction rate constant of all four individual reactions are equal is 584 K; at a heating rate of 0.1 K s^{-1} the reaction temperature ranges of all four individual reactions overlap and the temperature at which the maximum rate, i.e. the maximum value of the temperature derivative in the plot of $\mathrm{d}\alpha/\mathrm{d}T$ versus T, of all four individual reactions occurs is 600 K. These parameters have been used earlier by Flynn [3] and Agrawal [1,4] to study the behavior of single-step complex reactions.

TABLE 1

Values of A and E used for individual reactions

Reaction	A (s^{-1})	E (kcal mol^{-1})
1	2.4×10^{4}	19.1
2	4.5×10^{11}	38.2
3	6.1×10^{18}	57.4
4	7.4×10^{25}	76.5

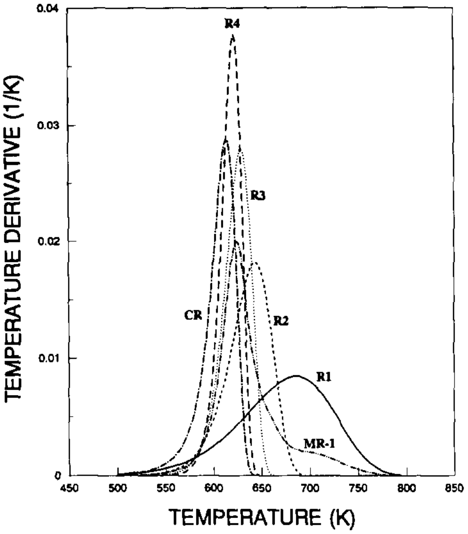


Fig. 1. Temperature derivative vs. temperature for individual reactions (R_i) (Arrhenius parameters shown in Table 1) and the resulting competitive reaction (CR) and multiple reaction (MR-1), assuming $g_1 = g_2 = g_3 = g_4 = 0.25$, at a heating rate of 1 K s^{-1}.

At temperatures below the isokinetic temperature, the low E reaction dominates the overall reaction; at the isokinetic temperature the rates of individual reactions are equal; and at temperatures above the isokinetic temperature the high E reaction dominates the reaction. The behavior of the complex reactions can then be studied by varying the reaction conditions such that the overall reaction occurs below the isokinetic temperature, at the isokinetic temperature or above the isokinetic temperature. By varying the heating rate it is possible to change the reaction temperature; and, depending on the heating rate, the nature of the overall reaction will be different.

Figure 1 summarizes the temperature derivative ($d\alpha/dT$) of individual reactions as a function of temperature at a heating rate of 1 K s^{-1}. At this heating rate the reactions occur above the isokinetic temperature, therefore the temperature derivative curves do not overlap. The peak amplitude of the temperature derivative curve is proportional to A/β; therefore, for a simple reaction with a single E, by increasing the heating rate the peak amplitude can be decreased and vice versa. Because the area under the curve remains the same (for a simple reaction), an increase in heating rate also results in an increase in the peak width. Therefore, an increase in the heating rate results in an increase in not only the reaction temperature but also in the reaction temperature range. Consequently, with an increase in the heating rate the peak becomes shorter and broader. These effects have been demonstrated by Flynn [3].

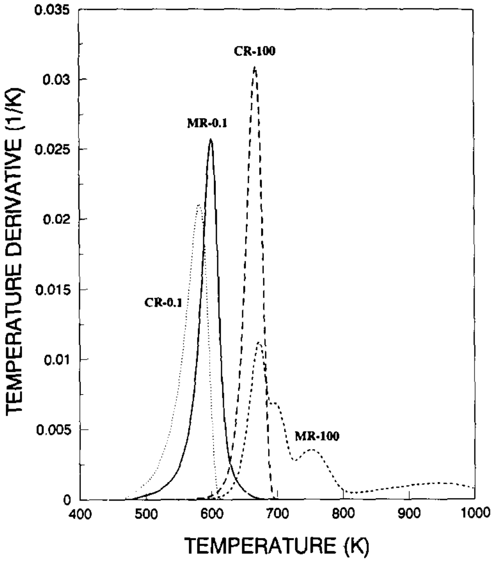


Fig. 2. Temperature derivative vs. temperature for competitive reactions (CR) and multiple reactions (MR) (assuming $g_1 = g_2 = g_3 = g_4 = 0.25$) at heating rates of 0.1 and 100 K s^{-1}. The data for the individual reaction are given in Table 1.

Also shown in Fig. 1 are the temperature derivatives of the overall competitive reaction and the overall multiple reaction. For the multiple reaction it is assumed that $g_1 = g_2 = g_3 = g_4 = 0.25$. The temperature range in which the multiple reaction occurs is bounded by the temperature of the individual reactions. The multiple reaction occurs over the entire temperature range of the individual reactions and thus the peak is broader than any of the individual reactions. The tail of the multiple reaction curve may be mistaken as a trend of a higher order reaction at this heating rate. The competitive reaction occurs at a lower temperature than any of the individual reactions.

The multiple reaction can exhibit multiple peaks (indicating non-Arrhenius behavior of the overall rate constant) depending on the rates of individual reactions, the heating rate and g_i. These effects are demonstrated in Figs. 2 and 3. Fig. 2 is a plot of the temperature derivative as a function of temperature for both competitive reaction (CR) and multiple reaction (MR) at heating rates of 0.1 and 100 K s^{-1}. An increase in the heating rate results in shifting the competitive reaction to higher temperatures. However, the peak amplitude of the competitive reaction increases and the peak width decreases with an increase in heating rate. Because an increase in the heating rate of a simple reaction results in a decrease in the peak amplitude and an increase in the peak width, this reflects a change in both E and A for the competitive reaction. The increase in peak amplitude and decrease in peak width for the competitive reaction indicates that

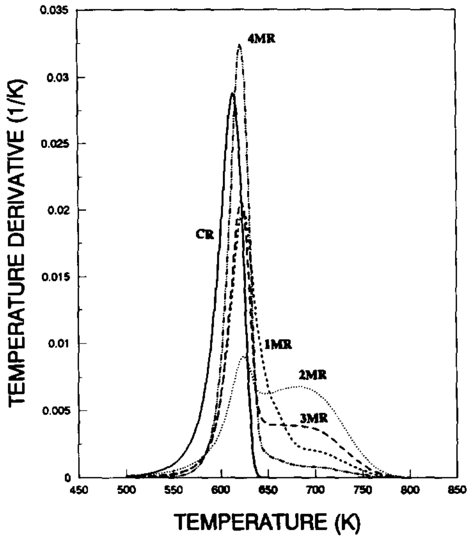


Fig. 3. Temperature derivative vs. temperature for competitive reaction (CR) and multiple reactions (MR) at a heating rate of 1 K s^{-1}. Data for multiple reaction cases are given in Table 2, and data for the individual reactions are given in Table 1.

both A and E increase with an increase in the heating rate. This is consistent with the fact that higher heating rates (also implying higher reaction temperatures) favor higher E value reactions. Therefore, both the A and E values of a competitive reaction are functions of heating rate. Earlier, Agrawal [4] had shown that E for the overall competitive reaction reflects the average of the individual E_i, if the individual reaction rates are comparable; and, if the rates of the individual reactions are significantly different, then the overall E value reflects the value of E_i of the most dominating reaction or reactions.

Also shown in Fig. 2 is the temperature derivative as a function of temperature for the overall multiple reaction at heating rates of 0.1 and 100 K s^{-1}. For the multiple reaction (MR) case, it is assumed that $g_1 = g_2 = g_3 = g_4 = 0.25$. The low E reaction dominates the kinetics at low heating rates and low temperatures (below the isokinetic temperature); and the high E reaction dominates at faster heating rates and high temperatures (above the isokinetic temperature). These effects are demonstrated in Fig. 2. At a heating rate of 0.1 K s^{-1}, the rates are comparable and it is difficult to observe the individual reactions occurring in the multiple reaction mixture. However, if the heating rate is increased to 100 K s^{-1} (and therefore increasing the reaction temperature to where the rates are no longer equal) the individual reactions occurring in the multiple reaction mixture can be separated. Flynn [3] has shown that low E and high E reactions can be separated from one another by varying the heating rates such that the reaction temperatures are significantly different from the

TABLE 2

Summary of g_i values used to calculate temperature derivative curves in Fig. 3

g_i	Multiple reaction mix case no.			
	1MR	2MR	3MR	4MR
1	0.25	0.80	0.45	0.10
2	0.25	0.05	0.05	0.05
3	0.25	0.05	0.05	0.05
4	0.25	0.10	0.45	0.80

isokinetic temperature. However, if the rates are of the same order of magnitude, i.e. when the reaction temperature is in the vicinity of the isokinetic temperature, the reactions cannot be separated. Thus the variation in heating rate is a useful tool in understanding the behavior of complex reactions.

Varying the heating rate by about three orders of magnitude is a problem in current thermal analysis devices, however, using non-traditional devices such as Curie-point pyrolyzers and electrically heated wire-mesh pyrolyzers, the heating rate can be varied over 4–5 orders of magnitude [11].

The nature of the multiple reaction is also a function of the initial composition of the individual reactants in the reaction mixture. This effect is demonstrated in Fig. 3. The heating rate used in this calculations was 1 K s^{-1}. For the multiple reaction case, the g_i values are summarized in Table 2 and the Arrhenius parameters are listed in Table 1.

The studies of Agrawal [4] have shown that the value of E for the overall multiple reaction depends not only on the individual rates but also on the initial composition of the reaction mixture; this effect is demonstrated in Fig. 3.

Some work has also been reported on modeling the overall reactions by varying the "pseudo" order of reaction and the activation energy as a function of conversion for multiple-independent reactions. Comparison of curves MR-1 (Fig. 1) and MR-0.1 and MR-100 (Fig. 2) indicates that modeling multiple reaction with the "pseudo" order of reaction approach has limited applications because the results are not capable of explaining the effect of heating rate. Curves 1MR, 2MR, 3MR and 4MR in Fig. 3 indicate that the pseudo order of reaction approach is also not capable of explaining the changes in the composition of the reaction mixture. Some work has also been published on modeling the overall multiple reaction for Avrami–Erofeev type equations. The studies of Brown and Galwey [12], Criado et al. [13] and Agrawal [14] indicate that Avrami–Erofeev type equations may not be applicable to non-isothermal kinetic studies, even for simple reactions. Therefore the use of the pseudo order of reaction approach and/or Avrami–Erofeev type equations is of little significance for understanding the behavior of complex reactions and only satisfies mathematical curiosity.

Sequential reaction

Very little work has been reported in the area of sequential reactions. Heide et al. [5] were perhaps one of the first groups of researchers to simulate the kinetics of sequential reactions. The sequential reaction scheme is represented as

$$\mathbf{a} \xrightarrow{k_1} \mathbf{b} + \mathbf{v} \xrightarrow{k_2} \mathbf{c} + \mathbf{v} \ldots \xrightarrow{k_i} \mathbf{j} + \mathbf{v}$$

The reactant is represented by **a**, and the products by **b**, **c**,..., **j**, and **v**; **v** is used to represent the volatile or gaseous products that escape from the condensed phase reaction matrix. The rate expressions for the sequential reactions are

$$\mathrm{d}a/\mathrm{d}T = -(A_1/\beta)a \exp(-E_1/RT) \tag{6}$$

$$\mathrm{d}b/\mathrm{d}T = (A_1/\beta)a \exp(-E_1/RT) - (A_2/\beta)b \exp(-E_2/RT) \tag{7}$$

$$\mathrm{d}v/\mathrm{d}T = (A_1/\beta)a \exp(-E_1/RT) + (A_2/\beta)b \exp(-E_2/RT) + \ldots \tag{8}$$

The study in this paper is limited to two first-order sequential reactions. Solutions of the above equations assuming that at time = 0 ($T = T_0$) $a = 1$ and $b = 0$ are

$$a = \exp[-(A_1/\beta)p(x_1)] \tag{9}$$

$$b = (A_1/\beta)I_\mathrm{k} \exp[(-A_2/\beta)p(x_2)] \tag{10}$$

where

$$I_\mathrm{k} = \int \exp[-E_1/RT - (A_1/\beta)p(x_1) + (A_2/\beta)p(x_2)]\ \mathrm{d}T \tag{11}$$

I_k is the "Kopplungs Integral" referred to by Heide et al. [5]. For this study, the $p(x)$ function was calculated by using the Agrawal approximation [15] and I_k was calculated by Simpsons approximation.

The Arrhenius parameters chosen for the study of sequential reactions are listed in Table 1. The reactions chosen were $E = 19.1$ kcal mol^{-1} and $E = 76.5$ kcal mol^{-1} with their corresponding frequency factors. Two cases of a sequential reaction scheme are discussed: Case 1, $E_2 > E_1$ and Case 2, $E_1 > E_2$. The sequential reactions occurring in the temperature range close to the isokinetic temperature, for either of these cases, simulate the behavior of a sequential reaction where $E_1 = E_2$.

Figures 4 and 5 summarize the results on the effect of heating rate on the sequence of a low E value reaction followed by a high E value reaction. The Arrhenius parameters are shown in Fig. 4. The effect of

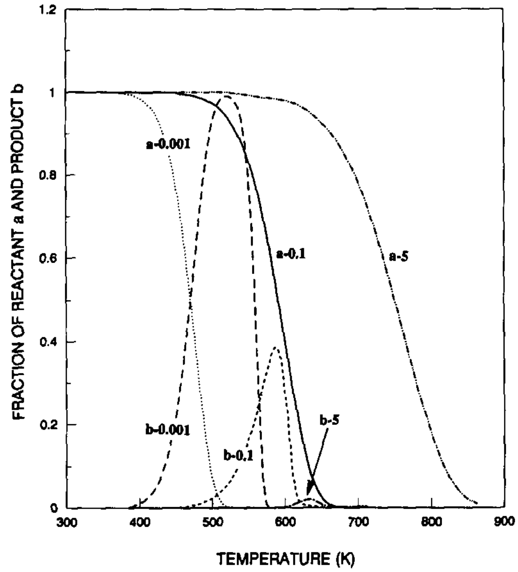


Fig. 4. Fraction of reactant **a** and product **b** as a function of temperature at heating rates of 0.001, 0.1 and 5 K s^{-1}. Arrhenius parameters are: $A_1 = 2.44E+04$ s^{-1}, $E_1 = 19.1$ kcal mol^{-1}; and $A_2 = 7.4E+25$ s^{-1}, $E_2 = 76.5$ kcal mol^{-1}.

heating rate on the decomposition of reactant **a** (lower E reaction) is the trend noticed for a first-order reaction, i.e. a shift to higher temperature and an increase in reaction temperature range with an increase in the heating rate. The amount of **b** present as a function of temperature at

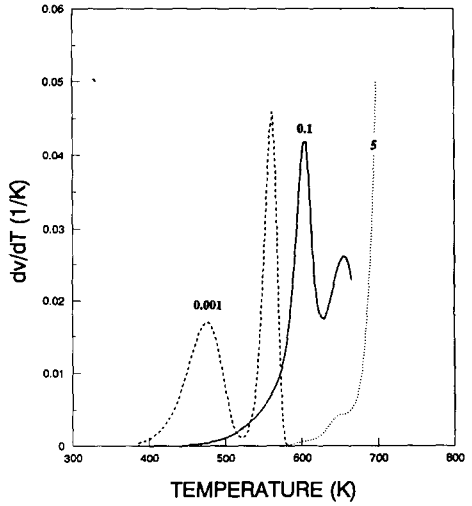


Fig. 5. Rate of volatile evolution by the sequential reaction. Arrhenius parameters are given in Fig. 4.

various heating rates is also shown in Fig. 4. At the low heating rate of 0.001 K s^{-1}, **b** (higher E reaction) reacts very slowly and the decomposition of **b** takes place after all of the reactant **a** has disappeared. Most of the reaction occurs at temperatures below the isokinetic temperature, therefore the high E reaction (decomposition of **b**) is the rate-limiting step at the slow heating rate of 0.001 K s^{-1}. At a moderate heating rate of 0.1 K s^{-1}, the formation and decomposition of **b** occur simultaneously; and, the reaction occurs at temperatures in the vicinity of the isokinetic temperature. At a heating rate of 5 K s^{-1}, the reaction occurs at temperatures above the isokinetic temperature, and therefore, the decomposition of **b** is rapid when compared to the decomposition reaction of **a**. At this high heating rate the rate-limiting step in the reaction sequence is the low E decomposition reaction of **a**.

The effect of heating rate on the rates of volatile evolution (or the weight-loss step) in a sequential reaction scheme where $E_2 > E_1$ is shown in Fig. 5. The effect of heating rate on the rate-controlling step can be visualized from Fig. 5. Evolution of the volatiles occurs in two steps; the initial peak is from the decomposition of the reactant **a** and the second peak is due to the decomposition of product **b**. At a low heating rate of 0.001 K s^{-1}, where the reactions occur below the isokinetic temperature, the two peaks are distinct. At a heating rate of 0.1 K s^{-1}, where the reactions occur in the vicinity of the isokinetic temperature, volatile evolution from the decomposition of both reactant **a** and product **b** are also seen. The second peak due to decomposition of **b** is interesting. After reaching the second maximum, the rate of volatile evolution suddenly drops to zero due to rapid depletion of **b** at high temperature. This is because at the end of the reaction, the reaction temperature is significantly above the isokinetic temperature and the high E reaction (decomposition of **b**) accelerates to completion. At a heating rate of 5 K s^{-1} the reactions occur above the isokinetic temperature. The first peak is visible as a hump, whereas the volatile evolution from **b** goes off scale and then drops instantaneously to zero. At a heating rate of 5 K s^{-1}, this reaction scheme exhibits a trend close to a zero-order reaction, whereas at a lower heating rate it exhibits characteristics of a complex reaction.

Fig. 5 demonstrates the effect of heating rate on a low E reaction followed by a high E reaction. At a low heating rate where the reaction occurs below the isokinetic temperature, the low E reaction is faster and the high E reaction is the rate-limiting step. At a high heating rate where the reaction occurs above the isokinetic temperature, the high E reaction is faster and the low E reaction is the rate-limiting step. At a moderate heating rate where the reaction occurs in the vicinity of the isokinetic temperature, the rates of both the low E and high E reactions are approximately equal and no single reaction is rate-limiting. At high heating rates where $E_2 > E_1$, the overall reaction may exhibit a pseudo zero-order

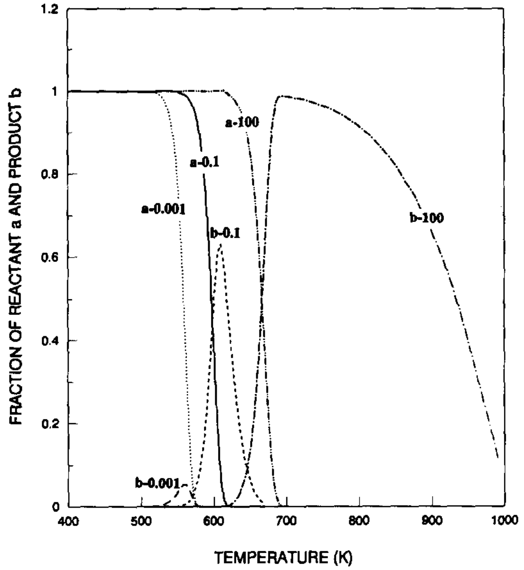


Fig. 6. Fraction of reactant **a** and product **b** as a function of temperature at heating rates of 0.001, 0.1 and 100 K s^{-1}. Arrhenius parameters are: $A_1 = 7.4E+25\ s^{-1}$, $E_1 = 76.5$ kcal mol^{-1}; and $A_2 = 2.44E+04\ s^{-1}$, $E_2 = 19.1$ kcal mol^{-1}.

reaction. The results of this study can be extended to the case where no weight loss occurs in either the decomposition of **a** or **b**. In such a case, the first peak (decomposition of **a**) or the second peak (decomposition of **b**) will not be seen (depending on which reaction is assumed not to loose weight) and the effect of heating rate on the behavior of the weight loss curve will be more drastic.

Figures 6 and 7 summarize the effect of heating rate on the sequence of a high E reaction followed by a low E reaction. The Arrhenius parameters are given in Fig. 6 and are the same as used in Figs. 4 and 5, except that the order is reversed. The effect of heating rate on the decomposition reaction of **a** is the same as that of a single first-order reaction. At the low heating rate of 0.001 K s^{-1} where the reactions occur below the isokinetic temperature, very little **b** is present in the reaction mixture during the reaction; this indicates that the reaction is limited by the high E decomposition reaction of **a**. At a heating rate of 0.1 K s^{-1}, where the reactions occur in the vicinity of the isokinetic temperature, the sequential reaction is not limited by a single reaction. At the higher heating rate of 100 K s^{-1} where the reaction occurs above the isokinetic temperature, the decomposition reaction of **b** is very slow and is the rate-limiting step of the reaction sequence.

The rate of volatile evolutions due to decomposition of **a** and **b** is shown in Fig. 7. At the low heating rate of 0.001 K s^{-1} where the reactions occur below the isokinetic temperature, the volatile evolution is in the form of a

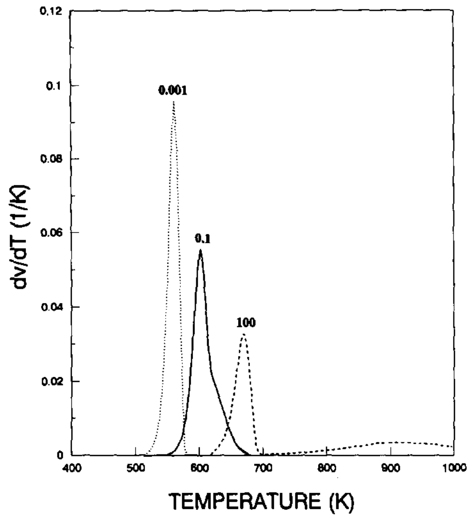


Fig. 7. Rate of volatile evolution by the sequential reaction. Arrhenius parameters are given in Fig. 6.

single peak, indicating a single reaction. At the moderate heating rate of 0.1 K s^{-1} where the reactions occur in the vicinity of the isokinetic temperature, the sequential reaction still presents a single curve. The tail indicates the change in the rate-limiting reaction and that the two reactions can be separated by increasing the heating rate. The shape of the tail also indicates a higher order of reaction. At the high heating rate of 100 K s^{-1} where the reaction occurs above the isokinetic temperature, the two reactions can be separated. The first peak due to decomposition of **a** is clear, followed by a slow rate of volatile evolution, indicating that the reaction is limited by the low E decomposition reaction of **b**. Thus comparison of Figs. 5 and 7 indicates that it is easier to identify the sequential nature of the reaction if a low E reaction is followed by a high E reaction when compared to the reaction sequence in which a high E reaction is followed by a low E reaction.

CONCLUSIONS

The behavior of a complex reaction, for both single-step and sequential reactions, is a function of the Arrhenius parameters of the individual reactions and the reaction temperature range. The isokinetic temperature provides a useful reference point to study the effect of heating rate on complex reactions. At temperatures below the isokinetic temperature, the low E reaction dominates; at the isokinetic temperature all reactions are in competition; and at temperatures above the isokinetic temperature, the high E reaction dominates. Thus the nature of the complex reaction varies with the reaction temperature.

The multiple heating rate technique and plots of temperature derivatives versus temperature provide useful information on the nature of the reactions. For a simple reaction, an increase in the heating rate causes a decrease in the peak amplitude and an increase in the peak width. But for a complex reaction, an increase in the heating rate may cause an increase in the peak amplitude and a decrease in the peak width. For competitive reactions, Flynn [3] has shown that at low heating rates and low temperatures, the low E reaction with its low broad peaks dominates. At fast heating rates and high temperatures, the high E reaction with tall, sharp peaks takes over. In the region of the isokinetic temperature, i.e. at moderate heating rates, the two processes are in even competition and the peak amplitude goes through a minimum.

The nature of the multiple reaction is a function of the rates of the individual reactions, the heating rate and the initial composition of the reaction mixture. Depending on the heating rate and/or the initial composition of the reaction mixture, the multiple reaction may exhibit various pseudo orders of reaction and/or even multiple peaks. Thus modeling multiple reaction with the "pseudo" order of reaction approach contributes little to the understanding of the behavior of complex reactions.

For the sequential reaction scheme where a low E reaction is followed by a high E reaction, the overall reaction generally exhibits multiple peaks. At low heating rates and at temperatures below the isokinetic temperature, the high E reaction is rate-limiting; at moderate heating rates and at the isokinetic temperature both reactions are in competition; and, at high heating rates and at temperatures above the isokinetic temperature, the low E reaction is rate limiting. At this high heating rate the reaction exhibits a pseudo zero-order reaction.

For the sequential reaction scheme where a high E reaction is followed by a low E reaction, the overall reaction generally exhibits a single reaction. Only at very high heating rate and at temperatures considerably above the isokinetic temperature, can the reaction be separated into individual reactions. As the heating rate is increased, the reaction order for the sequential reaction scheme where $E_1 > E_2$ appears to increase and is very similar in behavior to the multiple reaction scheme. From an analysis viewpoint, a sequential reaction is easier to identify when a low E reaction is followed by a high E reaction, compared to when a high E reaction is followed by a low E reaction.

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