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Kinetic analysis of complex decomposition reactions using evolved gas analysis

John P. Sanders · Patrick K. Gallagher

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Abstract For complex decomposition reactions, traditional methods, such as TG and DSC cannot fully resolve all of the steps in the reaction. Evolved gas analysis (EGA) offers another tool to provide more information about the decomposition mechanism. The decomposition of sodium bicarbonate was studied by TG, DSC and EGA using a simultaneous thermal analysis unit coupled to a FTIR. The decomposition of sodium bicarbonate involves two reaction products H_2O and CO_2, which are not evident from either TG or DSC measurements alone. A comparison of the reaction kinetics from TG, DTG and EGA data were compared.

Keywords Evolved gas analysis · Kinetic analysis · Simultaneous TG/DSC · Transfer time

Introduction

This work was undertaken to determine if data from evolved gas analysis (EGA) could be used for the kinetic analysis of complex decomposition reactions. Traditionally, TG and DSC have been used to study the kinetics of simple decomposition reactions. When multiple decomposition products are involved, complicated deconvolution procedures were required to separate the contribution of each reaction product. EGA data offers the potential to simplify the analysis of complex decomposition reactions since the evolution of various reaction products can be followed separately.

When working with EGA, there is a finite transfer time which is the time that it takes for the gas evolved from the sample to reach the gas analyzer. The transfer time is influenced by the flow rate of the gases, volume of the gas cell, transfer line and furnace, and the flow profile through the system [1]. Directly coupled thermal analyzers utilizing either Fourier transform infrared spectroscopy (FTIR) or mass spectrometry (MS) which have been designed to minimize the effect of transfer time have been described by Kaisersberger and Post [1].

In addition to instrumental design, several operating parameters can influence the transfer time. Higher flow rates reduce the transfer time but increase dilution [2]. The detection limit of the EGA to the gases involved in the reaction must also be considered. For FTIR analysis, excessive dilution may reduce the minimum detection limit for weakly absorbing species to an unacceptable level. Also when using an FTIR, the spectral resolution and number of co-added scans determine the time resolution of the evolved gas data [2]. It is also important to note that calibration of EGA data is required to obtain quantitative results [3]. In most cases, calibration of the EGA signal is not required since it is used in conjunction with Thermogravimetric (TG) or Differential Scanning Calorimetry (DSC) data.

Various authors have used the difference between the DTA or DTG peak temperature and the corresponding evolved gas peak to quantify the transfer time [4, 5]. This differential can be used to select experimental conditions that minimize the effect of transfer time.

The decomposition of $NaHCO_3$ has been studied by several investigators [3, 6–10]. The reaction proceeds according to the following path (Eq. 1) with the

J. P. Sanders (✉)
The National Brick Research Center, Clemson University,
100 Clemson Research Blvd, Anderson, SC 29625, USA
e-mail: jpsand@clemson.edu

P. K. Gallagher
Clemson University, Anderson, SC, USA

P. K. Gallagher
The Ohio State University, Columbus, OH, USA

simultaneous evolution of CO_2 and H_2O [6]. The decomposition rate is dependent on the partial pressure of both CO_2 and H_2O [7, 8]. In controlled rate EGA studies, Yamada and Koga found that increasing the partial pressure of CO_2 retards the rate of reaction [7]. Conversely, increasing the partial pressure of H_2O appears to enhance the reaction rate [7]. The decomposition rate is also affected by self cooling due to the endothermic nature of this reaction. Given the simultaneous evolution of CO_2 and H_2O, sodium bicarbonate was selected to study the possibility of using EGA data for kinetic analysis.

$$2NaHCO_{3(s)} \rightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)} \qquad (1)$$

Values for the activation energy of this reaction range from approximately 90 to 120 kJ mol^{-1} depending on the experimental conditions and the computational techniques used to model the experimental data [9, 10]. Several studies have found that the decomposition kinetics can be modelled adequately with a simple first order reaction, while other investigators have applied more complicated models [9–11]. The experimental conditions and computational methods used to interpret the experimental data have a profound effect on the determination of the kinetic parameters [11].

Experimental

The sodium bicarbonate used in this study was a commercial grade produced by Church and Dwight. The material was screened to remove particles greater than 74 µm. Simultaneous TG/DSC measurements were made on a Netzsch STA 449C which was coupled to a Brucker Vector 22 FTIR. The details of the coupling of the thermal analyzer and the FTIR have been described by Kaiserberger and Post [1]. Simultaneous TG, DSC and EGA measurements were obtained at heating rates of 1, 2, 4, 8, and 16 °C min^{-1}. A flow rate of 100 mL min^{-1} of nitrogen was used for all experiments. Open alumina crucibles were used in these measurements. The sample size ranged from 20 ± 0.5 mg. The DSC sensitivity curve was determined for each heating rate using a sapphire disk.

In this study, a resolution of 4 cm^{-1} was used for all measurements. The number of co-added scans was reduced for the faster heating rates to improve the time resolution of the evolved gas data from the FTIR. These conditions, along with the nitrogen flow rate were selected to minimize the transfer time between the thermal analyzer and the FTIR. The CO_2 and H_2O emission traces were determined by integrating the FTIR absorption spectra from 2,450 to 2,200 cm^{-1} for CO_2 and 2,200 to 1,600 cm^{-1} for H_2O. Netzsch Proteus and Thermokinetic software packages were used for data analysis [12–14].

Results and discussion

A typical decomposition profile is shown in Fig. 1 for a sample heated in nitrogen at the intermediate heating rate of 8 °C min^{-1} with a flow rate of 100 mL min^{-1}. The decomposition of $NaHCO_3$ was characterized by the simultaneous emission of CO_2 and H_2O as noted previously [6]. Additionally, the reaction was characterized by a large endotherm.

To evaluate the effect of the flow rate on the transfer time to the FTIR, this experiment was repeated at flow rates of 75 and 50 mL min^{-1}. The results of this comparison are summarized in Tables 1 and 2. Table 1 shows the effect of flow rate on the extrapolated onset temperature at a heating rate of 8 °C min^{-1} in the various flow rates. Table 2 shows the effect of the flow rate on the peak temperatures under the same conditions. For the TG data, the inflection point was used in place of the peak

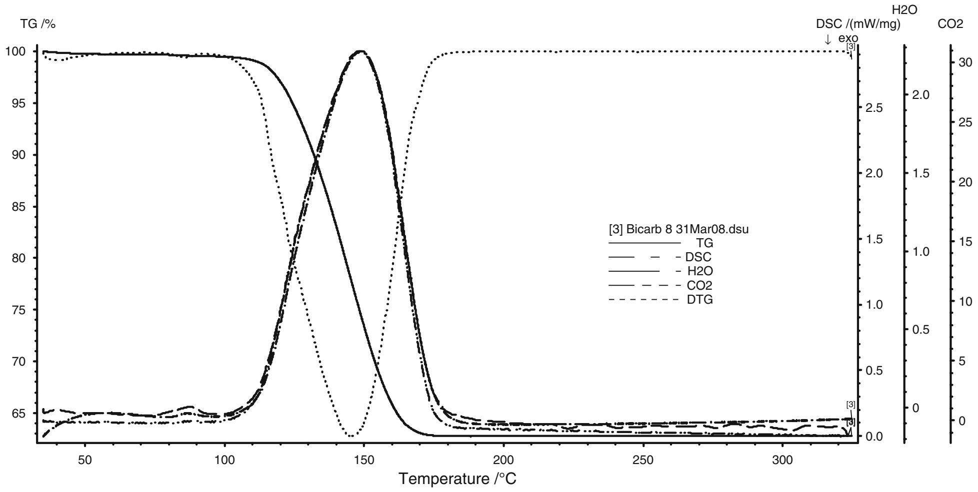


Fig. 1 Decomposition of $NaHCO_3$ (8 °C min^{-1})

Table 1 Effect of flow rate on extrapolated onset temperature at 8 °C min^{-1}

Flow rate	50 mL min^{-1}	75 mL min^{-1}	100 mL min^{-1}
TG data	123.4	123.6	123.4
DSC data	112.8	113.3	112.6
DTG data	110.8	111.8	110.7
CO_2 (EGA) data	112.3	112.0	111.6
H_2O (EGA) data	113.8	113.5	113.2

Table 2 Effect of flow rate on peak temperature at 8 °C min^{-1}

Flow rate	50 mL min^{-1}	75 mL min^{-1}	100 mL min^{-1}
TG data[a]	146.2	146.2	145.6
DSC data	149.3	148.8	148.7
DTG data	146.2	146.2	145.6
CO_2 (EGA) data	150.8	149.7	148.7
H_2O (EGA) data	150.8	149.7	148.7

[a] For the TG data, the inflection point was used

temperature in Table 2. No correction factors were applied to the onset and peak temperatures reported in Tables 1 and 2.

The extrapolated onset temperature for the TG data, was higher than for the other simultaneously collected data sets. The determination of the extrapolated onset temperature for the TG data gives a different result than the other data sets due to the shape of the TG curve relative to the other data sets as seen in Fig. 1. This effect is especially apparent when the onset temperature for the TG data and the derivative of the TG data (DTG) are compared. This difference is due to the mathematical amplification of sensitivity and noise made by differentiation. In other words, the delay between the TG and DTG data is the result of the calculation of the DTG from the TG data and is independent of the experimental conditions. For the other data sets, the delay between the decomposition event and the detection of the event by the appropriate sensor is due to the experimental conditions such as flow rate. The DSC, DTG and EGA data for CO_2 and H_2O emission all resulted in similar onset temperatures. In general, lower onset temperatures were observed with increasing flow rate, as would be expected, but the difference was very small.

Flow rate has a pronounced effect on the peak temperature as demonstrated in Fig. 3. For the EGA data, a wider range of peak temperatures was observed than for the TG, DSC or DTG data. At the highest flow rate of 100 mL min^{-1}, the peak temperature was similar for the DSC and EGA data. The TG and related DTG data displayed the lowest peak temperatures. It is again important to note that the inflection point was substituted for the peak temperature with the TG data. The highest flow rate appears to provide a minimum transfer time and was used in all subsequent measurements. In addition to the flow rate, the instrumental design and coupling system has been optimized to reduce the effect of transfer time [1]. As would be expected, flow rate had less of an effect on the DSC data than the EGA data although the differences between all of the data sets was very small.

The extrapolated onset temperatures as a function of heating rate for each data set are shown in Fig. 2. As noted previously, the extrapolated onset temperatures for the TG data were higher than the other data sets and different from the DTG curve. The other data sets including the EGA data sets for CO_2 and H_2O were very similar. At the highest heating rate, 16 °C min^{-1}, the extrapolated onset temperatures for the DSC, CO_2 and H_2O data sets were very similar, but the onset for the DTG data began to diverge. Similarly, the peak temperatures as a function of heating rate for each data set are shown in Fig. 3. Less scatter was

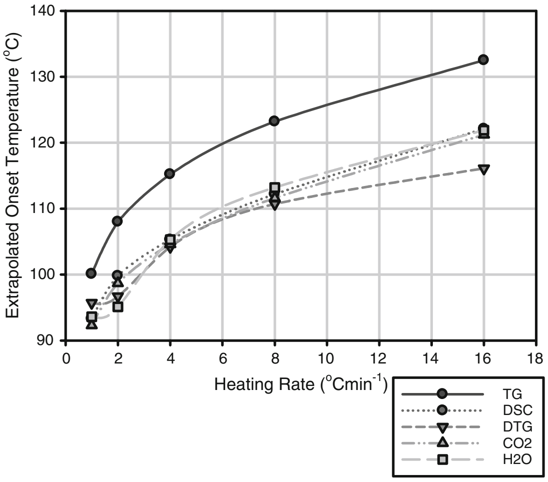


Fig. 2 Comparison of onset temperatures

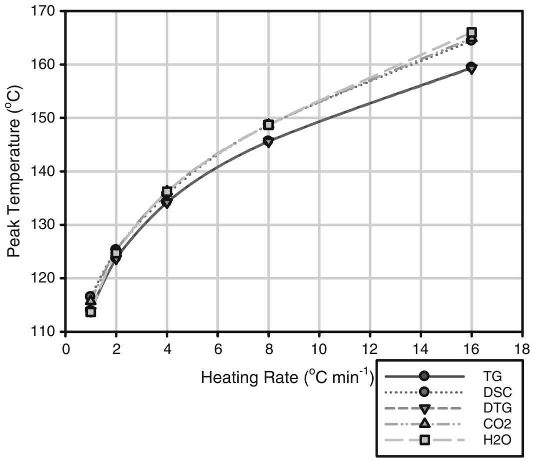


Fig. 3 Comparison of peak temperatures

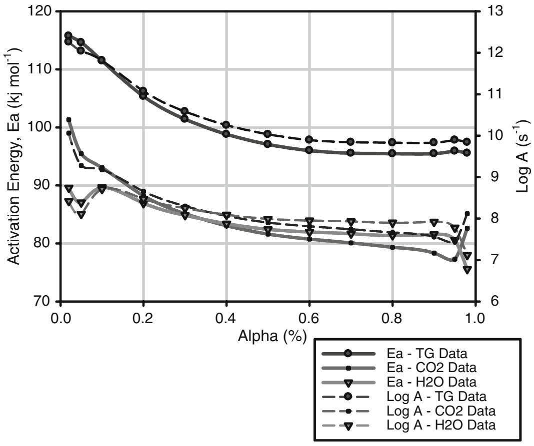


Fig. 4 Ozawa Flynn Wall model free kinetic analysis comparison (E_a—*solid lines*, Log A—*dashed lines*)

observed in the peak temperature data, but the difference between the TG and DTG data and the EGA data does seem to become somewhat more pronounced at the higher heating rates. It does not appear that the transfer time increases significantly with higher heating rates as might be expected, but the differences between the TG and DTG data sets and the DSC and EGA data sets become more significant as the heating rate increased.

The kinetic parameters for the TG, CO_2 and H_2O data sets were compared using the Ozawa Flynn Wall model free approach using the Netzsch Thermokinetics software package [12, 13]. The kinetics of the DSC data set were not considered due to the additional complication of the instrumental correction factor required by the software for DSC data [12]. This correction factor is designed to compensate for the thermal transport phenomena associated with DSC measurements [14, 15]. It should be noted that no correction factors have been applied to any of the data sets. Further, the DTG data was not considered in the model free kinetics comparison due to limitations with the software.

A comparison of the activation energy, E_a, and the pre-exponential term, log A, for the TG, CO_2, and H_2O data sets as a function of the fraction conversion, α, is displayed in Fig. 4. As can be seen, the TG data resulted in both a higher activation energy and pre-exponential term than the two EGA data sets. The TG data also exhibited a higher onset temperature and lower inflection point temperature than the EGA data sets as noted previously. The CO_2 and H_2O data sets resulted in very similar kinetic parameters. It is interesting to note the similarity between the shape of the E_a and log A curves for each data set, suggesting an inability to accurately resolve a distinct separation or independence between the two terms. This correlation or compensation effect was also noted by Janković and Adnađević in their study of the thermal decomposition of $NaHCO_3$ [10].

The reaction kinetics for the TG, DTG, CO_2 and H_2O data sets were also compared by fitting each data set to a generic *n*th order, Fn, reaction model. This fitting was accomplished, using the Netzsch Thermokinetics software package, to allow a direct comparison between the data sets. The data was fit over an α range of 0.0005–0.9995. A higher level of fitting could have been achieved for each data set using the non-linear regression capabilities of the Thermokinetics software package, but this was not done to allow for the comparison of the resulting kinetic parameters using a single reaction model [12]. Further, allowing multiple reaction steps, as recommended by Maciejewski would naturally have resulted in a higher level of correlation between the kinetic model and the experimental data [11]. The significance of these improved values with increasing variables always requires thoughtful consideration.

The results of the kinetic modelling for the TG, CO_2 and H_2O data sets using the *n*th order reaction model are illustrated in Figs. 5, 6 and 7, respectively. The quality of the fitting for each of these data sets is illustrated by the difference between the experimental data (symbols) and the prediction from the kinetic model (lines). It is clear that the quality of data fit, but not necessarily the meaningfulness, could have been improved with further kinetic modelling. Further, a summary of the kinetic model data using the *n*th order model is shown in Table 3 and Fig. 8. The coefficient of determination, R^2, is also reported for each of the models in Table 3. The best fit, using the *n*th order reaction model, was achieved for the TG data set, while the CO_2 and H_2O data sets achieved a lower level of fit. For the TG data, shown in Fig. 5, the inclusion of a second reaction step would have helped to improve the fit for the initial part of the decomposition curve. The kinetic modelling of the CO_2 and H_2O data sets, shown in Figs. 6 and 7, would have benefited from at least one more reaction step, but multiple reaction steps would likely be required to achieve a higher level of correlation with the experimental data.

Similar to the model free kinetic analysis described in Fig. 6, the kinetic modelling using the *n*th order model yielded kinetic parameters which appear to show the kinetic compensation effect [10]. The compensation effect for the kinetic parameters is very evident in Fig. 8. The compensation effect makes a direct comparison of the results of the kinetic modelling for each data set difficult. Previous work by Sanders and Gallagher attempting to

Fig. 5 Kinetic modelling of TG data (*n*th order, single step reaction)

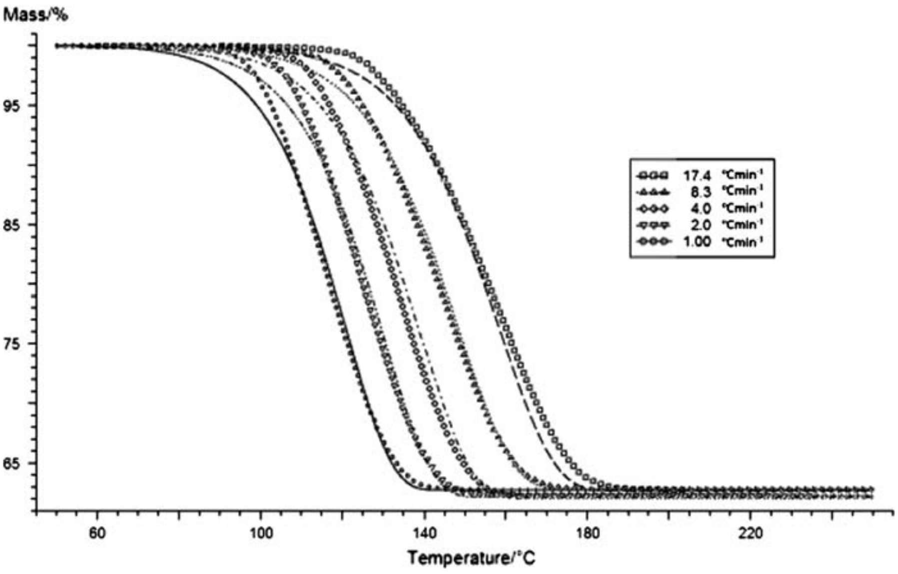


Fig. 6 Kinetic modelling of CO_2 data (*n*th order, single step reaction)

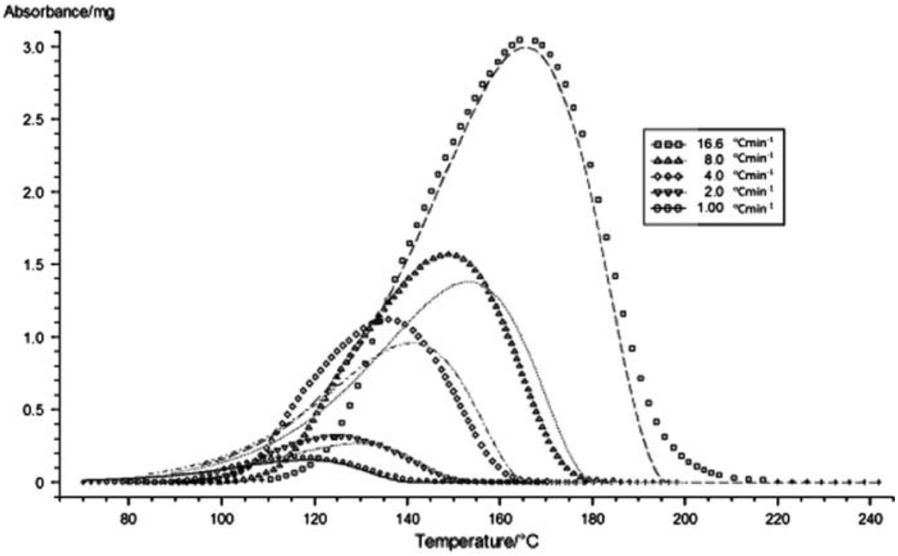


Fig. 7 Kinetic modelling of H_2O data (*n*th order, single step reaction)

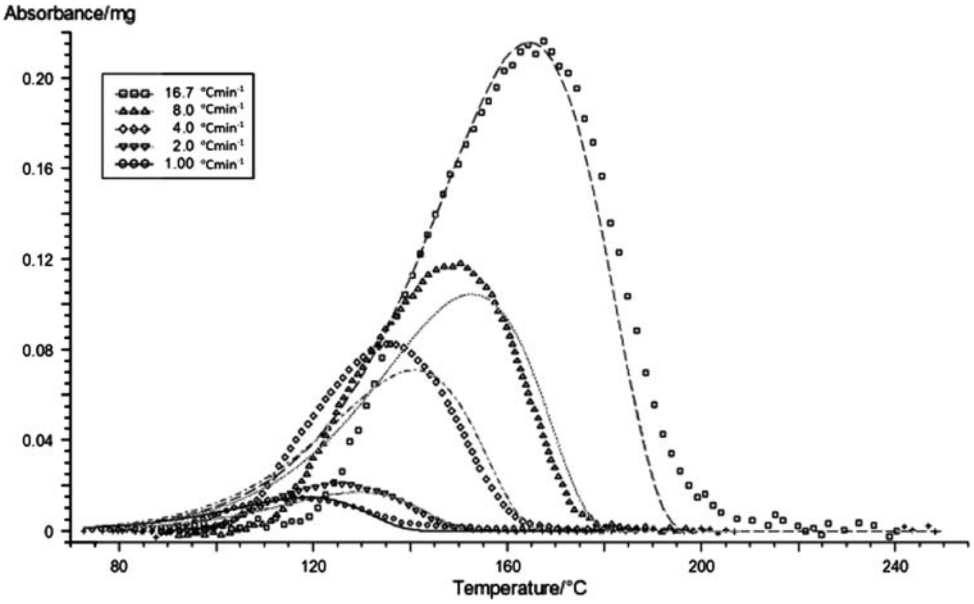


Table 3 Comparison of kinetic parameters

	TG	DTG	CO_2 trace	H_2O trace
Reaction model	*n*th order	*n*th order	*n*th order	*n*th order
Log A (s^{-1})	10.16	9.11	7.34	7.68
E (kJ mol^{-1})	98.54	90.23	77.36	79.98
Reaction order	0.85	0.90	0.77	0.80
R^2	0.998	0.988	0.970	0.974

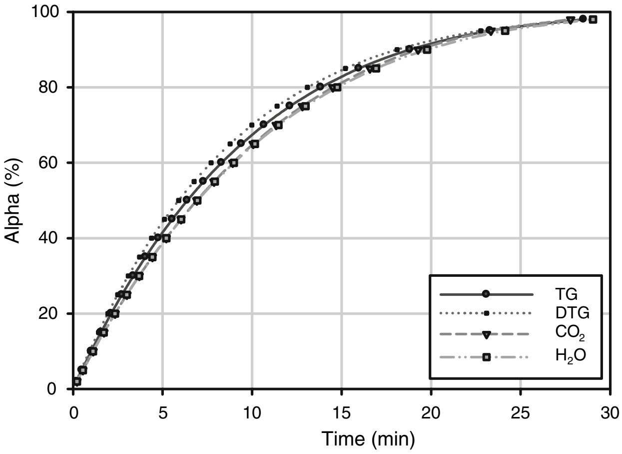


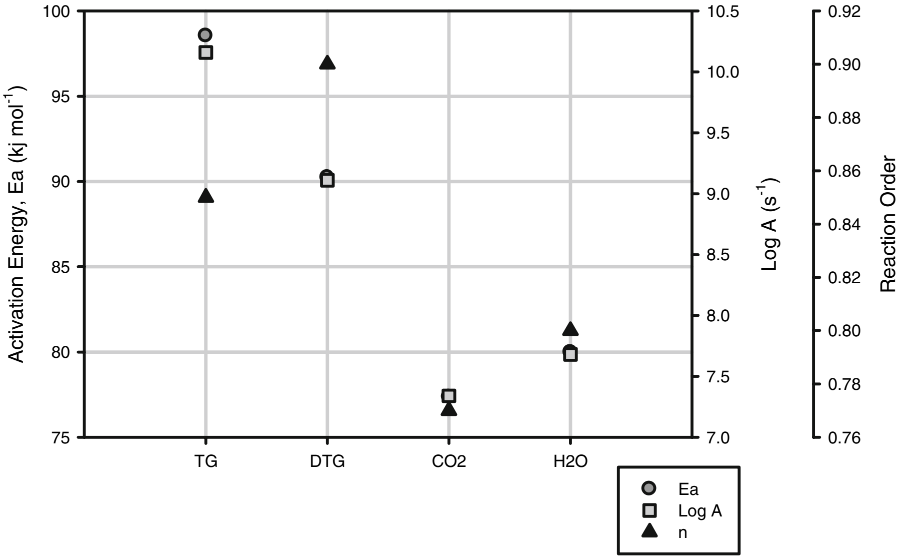
Fig. 9 Prediction of reaction rate at 125 °C

correlate kinetic modelling of simultaneous TG/DSC data for the decomposition of calcium carbonate also encountered this compensation effect [14, 15]. Both Brown and Galwey have also discussed similar problems with the current state of kinetic analysis of solid state decomposition reactions [16, 17]. Despite the lack of correlation in kinetic parameters between the various data sets due to the compensation effect, it is clear that each data set can be described by the *n*th order reaction model with a relatively high degree of correlation.

The kinetic parameters reported in Table 1, were used to predict the reaction rate at 125 °C as a means of comparing the modelling of each data set. The predictions determined by each of the kinetic models are shown in Fig. 9. The predictions based on each set of kinetic parameters were very similar. The calculated Arrhenius parameters must be taken as a pair rather than independently significant parameters which emphasizes the point of the compensation effect. The EGA data derived from the FTIR for the evolution of CO_2 and H_2O from the decomposition of $NaHCO_3$ were suitable for modelling the decomposition reaction. The transfer times required to move the gases from the thermal analyzer to the evolved gas analyzer do not seem to significantly impact the kinetic model.

For the decomposition of $NaHCO_3$, where the evolution of CO_2 and H_2O occur simultaneously, kinetic modelling with evolved gas data is relatively simple. In more complicated systems where multiple decomposition products are involved, the use of evolved gas data for kinetic modelling allows for the possibility of studying the reaction in much more detail than the traditional methods of thermal analysis, such as TG or DSC.

Fig. 8 Kinetic parameters (*n*th order reaction model)



Conclusions

- The transfer time for the detection of EGA signals can be minimized by using an adequate flow rate.
  - For weakly absorbing species, increasing the flow rate decreases the detection limit.
- The extrapolated onset temperatures for the EGA signals were lower than the onsets determined for the TG data and very similar to the onsets determined for the DTG data.
- Peak temperatures were general higher for the EGA data than for the TG or DTG data.
  - The delay in peak temperature for the EGA data appears to increase with increasing heating rate.
- Model Free Kinetic Analysis predicts a lower activation energy and pre-exponential term for the evolved gas data when compared to the TG data.
  - The activation energy and the pre-exponential term seem to closely follow each other, suggesting a lack of independence.
- Fitting the data to a single step *n*th order kinetic model resulted in an adequate fit for the TG, DTG and EGA data.
  - The fit of the EGA data resulted in lower activation energies, pre-exponential and reaction orders.
- The kinetic data for each data set predicted similar reaction rates at 125 °C.
  - EGA data were adequately able to predict reaction rates for this complex reaction.

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