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Comparison of some methods for activation energy determination of thermal decomposition reactions by thermogravimetry

R.R. Keuleers, J.F. Janssens, H.O. Desseyn*

Chemistry Department, Antwerp University (RUCA), Groenenborgerlaan 171, B2020 Antwerp, Belgium

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Abstract

The activation energy for the thermal decompostion of chemical compounds can be determined using isothermal or non-isothermal TGA measurements or by using the recently introduced modulated TGA method (MTGA, TA Instruments). In the course of our investigation on the decompostion of complexes, we started a comparative study of different measurement and calculation procedures for the thermal decompositon of $Mn(Urea)_2Cl_2$. As a reference, we did the same study on the sublimation of *N*-*n*-propyloxamide. The results of our comparative study on the determination of the activation energy for the decomposition/sublimation of these compounds are given. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Activation energy; Isothermal TGA; Non-isothermal TGA; Modulated TGA

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1. Introduction

Reaction kinetics has always been a point of interest for chemists: as early as 1889 S. Arrhenius proposed his well-known formula for the temperature-dependence of the reaction rate, and the first Nobel Prize in chemistry (in 1901) was awarded to J.H. Van't Hoff, who was doing research in reaction rates. Every year, several books and many articles about reaction rates and activation energy appear. Browsing through this vast amount of literature proves that up to now scientist do not agree about what is the best way to determine the activation energy for the thermal decomposition of solids. The calculation and the meaning of activation energy is always a subject for animated discussions at thermal analysis meetings (ICTAC, ESTAC, . . .). All this interest lies in the fact that the value of the activation energy can give an idea about the optimum reaction conditions in process chemistry, it gives an idea about the thermal stability and the expected lifetime of a compound to be kept at a certain temperature or it provides information in quality research.

In our research on the structure and stability of a number of ligands and their coordination compounds, the activation energy of the thermal decomposition reaction is an indication of the relative bond strengths within the molecules studied and can be related to vibrational frequencies determined from IR and Raman spectroscopy. We therefore tested several determination methods for the activation energy on one coordination compound ($Mn(Urea)_2Cl_2$) and on one ligand (*N*-*n*-propyloxamide).

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* Corresponding author. Tel.: +32-321-80-365;
fax: +32-321-80-233.
E-mail address: jojans@ruca.ua.ac.be (H.O. Desseyn).

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The complex compound $\mathrm{Mn(Urea)_2Cl_2}$ decomposes in two steps to $\mathrm{MnCl_2}$ according to the following reaction:

$$\mathrm{Mn(Urea)_2Cl_2} \rightarrow \mathrm{Mn(Urea)_1Cl_2} \rightarrow \mathrm{MnCl_2}$$

Since these two decomposition steps are well separated, it is a compound suited for this comparative study. In the first decompostion step, most of the released Urea sublimes but a side reaction can occur, namely the thermal decomposition of a small fraction of the free Urea to biuret, according to the following scheme:

$$\begin{aligned} &\mathrm{2H_2N{-}CO{-}NH_2(s)} \\ &\quad \rightarrow \mathrm{H_2N{-}CO{-}NH{-}CO{-}NH_2(s) + NH_3(g)} \end{aligned}$$

Below 175 °C, the fraction of Urea decomposing is neglectible. This was concluded from the fact that at the end of experiments involving temperatures below 175 °C a white compound was observed that was condensed on the outlet of the oven. IR-spectroscopy proved that this compound was Urea.

This side reaction becomes important at temperatures above 175 °C and this phenomenon gives the opportunity to study the influence of side reactions. As a comparison reaction we studied the heating of *N*-*n*-propyloxamide. TG, DTG and EGA measurements at slow heating rates (below 5 °C/min) show only one reaction: the sublimation of the compound without decomposition.

At higher heating rates (5–10 °C/min) not all of the compound has sublimed at 200 °C and in DSC we see a sharp endothermic peak (a melt) overlapping with the sublimation peak. At high heating rates (20 °C/min) we see a small melting peak followed by a broad endothermic peak. From DSC we calculated the total δH-value and for every heating rate between 3 and 20 °C/min we found a total reaction heat of about 100 kJ/mol, proving that there is no decomposition reaction and thus that the broad endothermic peak is due to the evaporation of the compound.

2. Experimental

The synthesis of $\mathrm{Mn(Urea)_2Cl_2}$ is described elsewere [1]. Thermogravimetric measurements were done on a TGA 2950 instrument from TA Instruments (New Castle, DE, USA) under a $\mathrm{N_2}$-stream of 100 ml/min. Sample size was about 15 mg for $\mathrm{Mn(Urea)_2Cl_2}$ and about 5 mg for *N*-*n*-propyloxamide.

3. Theoretical considerations and calculation procedures

Kinetic analysis of heterogeneous solid-state reactions always starts with the general formula for the reaction rate, v

$$v = \frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_\mathrm{T} f(\alpha) \tag{1}$$

The quantity α is the degree of conversion, $f(\alpha)$ is a mathematical function whose form depends on the reaction type and k_T is the temperature-dependent rate constant.

For the rate constant, we have no better alternative than the Arrhenius equation for homogeneous reactions: $k_\mathrm{T} = A\mathrm{e}^{-E_\mathrm{a}/(RT)}$, where A is the pre-exponential factor or frequency factor, E_a the activation energy and R the general gas constant, 8.314 J/mol K.

This gives the basic equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A f(\alpha)\, \mathrm{e}^{-E_\mathrm{a}/(RT)} \tag{2}$$

3.1. Isothermal measurements

Many authors restrict the mathematical function to $f(\alpha) = (1-\alpha)^n$, where n is called the reaction order in analogy with homogeneous reactions. Starting from isothermal measurements at different temperatures, we can then use a logarithmic form of this equation to calculate E_a and A from the resulting straight line.

$$\ln\left(\frac{(\mathrm{d}\alpha/\mathrm{d}t)_\mathrm{T}}{(1-\alpha)^n}\right) = \ln A - \frac{E_\mathrm{a}}{R}\frac{1}{T} \tag{3}$$

This calculation is repeated for different values of n and the value that gives the highest correlation coefficient is considered to be the best value. The slope and onset give us $-E_\mathrm{a}/R$ and $\ln A$, respectively.

Another procedures starts from the integrated form of Eq. (1).

$$F(\alpha) = \int_{\alpha 1}^{\alpha 2} \frac{\mathrm{d}\alpha}{f(\alpha)} = k_\mathrm{T} \int_{t1}^{t2} \mathrm{d}t = k_\mathrm{T} t \tag{4}$$

Plotting $F(\alpha)$versus time with the right form of $f(\alpha)$ will yield a straight line whose slope gives k_T for that temperature. If we repeat the measurement and the calculation for other temperatures, we can plot ln k_T as a function of $1/T$. This will give us a straight line with slope $-E_a/R$ and onset $\ln A$, if we accept $k_T = A e^{-E_a/(RT)}$ for like homogeneous reactions.

3.2. Non-isothermal measurements

3.2.1. Linear heating rates

If we perform non-isothermal measurements with a linear heating rate $\beta = dT/dt$, the basic Eq. (2) can be written as

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha)\, e^{-E_a/(RT)}$$

Restricting the function to $f(\alpha) = (1-\alpha)^n$ and taking logarithms, we get

$$\ln\left(\frac{d\alpha}{dT}\right) = \left[n \ln(1-\alpha) + \ln\left(\frac{A}{\beta}\right)\right] - \frac{E_a}{RT} \tag{5}$$

Kofstad [2] transforms this equation to

$$\ln\left(\frac{-d\,[\ln(1-\alpha)]}{dT}\right) + (1-n)\ln(1-\alpha) = \ln\frac{A}{\beta} - \frac{E_a}{R}\frac{1}{T}$$

From a single measurement (one value of β) we can, for each value of α, calculate the left hand side of the equation for several values of n.

The value of n giving the best correlation coefficient for the resulting straight line is used, and from the slope of that line E_a is calculated.

Ingraham and Marrier [3] complicate the formulae by suggesting that the frequency factor A is a linear function of temperature ($A = A' \times T$), but they restrict the value of n to zero. Eq. (5) can then be transformed to

$$\ln\left(\frac{\beta}{T}\right)\frac{d\alpha}{dT} = \ln A' - \frac{E_a}{RT}$$

If we do not restrict the reaction mechanism to zeroth order, we get

$$\ln\left(\frac{\beta}{T}\right)\frac{d\alpha}{dT} - \ln(1-\alpha) = \ln A' - \frac{E_a}{RT}$$

Freeman and Carroll [4] start from Eq. (5) for two values of α and obtain the following equation:

$$\frac{\Delta \ln(d\alpha/dT)}{\Delta \ln(1-\alpha)} = n - \frac{E_a}{R}\frac{\Delta(1/T)}{\Delta \ln(1-\alpha)}$$

Again, we start from one non-isothermal run to calculate the right hand side of the equation for a series of values of α, T and plot them against the left-hand side. The slope of the obtained straight line gives us E_a/R while the onset equals n.

The methods of Kofstad and of Ingraham and Marrier give us a value of n, if we accept the correlation coefficient of the obtained straight line as a valuable criterium. The method of Freeman and Carroll gives us n as the onset of the line.

These three methods use one single measurement and allow us to calculate E_a from the slope of a straight line, for a range of values of α. Here, it should be noted that changing the heating rate and thus the temperature at which the reaction takes place can change the reaction mechanism and thus the activation energy. Therefore methods based on only a single run (one heating rate) are disapproved of by most researchers.

The whole procedure can be repeated for other heating rates and in such a case a comparison of values obtained at different heating rates can give an indication if the values of E_a are trustworthy.

Friedman [5] writes Eq. (5) as

$$\ln(\beta)\frac{d\alpha}{dT} = \ln A + n\ln(1-\alpha) - \frac{E_a}{RT}$$

This method starts from different runs (at different heating rates) and let us calculate E_a for a fixed value of α, but from the onset we can not calculate A and determine a "good" value for n at the same time.

We can write Eq. (5) in seven different forms, always giving a straight line with $1/T$ as independent variable and $-E_a/R$ as slope. If we restrict the left hand side to $\ln(d\alpha/dT)$, $\ln \beta$, or $\ln[\beta(d\alpha/dT)]$, we do not need to know the form of $f(\alpha)$, but then we can calculate only E_a and not A.

In the case of the first possibility $\ln(d\alpha/dT) = \ln(Af(\alpha)/\beta) - E_a/(RT)$, we use data from one measurement (one linear heating rate β) and plot the left hand side of the equation as a function of $1/T$ for different values of α. Here too, we should remember the above-mentioned disadvantages of methods based on one measurement.

In the case of the second and third possibilities,

$$\ln\beta = \ln\left(\frac{Af(\alpha)}{(d\alpha/dT)}\right) - \frac{E_a}{RT} \quad \text{and}$$

$$\ln\left(\frac{\beta\, d\alpha}{dT}\right) = \ln(Af(\alpha)) - \frac{E_a}{RT}$$

we use data from measurements done at different heating rates and we calculate E_a for a fixed value of α. We can then repeat the calculation for other values of α.

3.2.2. Modulated heating rates

In a modulated heating rate method, a sinusoidal temperature modulation is superimposed on top of a conventional heating profile. This working method is equivalent to temperature-modulated DSC, and as a fact, both techniques were devised by Mike Reading, whereby MTGA is based on earlier work on the jump factor-method by Flynn [6] and Dickens [7]. The rate of weight loss responds to the temperature oscillations and the use of discrete Fourier transformation allows to calculate the kinetic parameters E_a and A on a continuous basis, making possible the study of the decomposition kinetics as a function of time, temperature and conversion factor, without any assumptions about the reaction mechanism (model-free calculations). The software calculates E_a on the basis of the following equation:

$$E_a = \frac{R(T^2 - A'^2)L}{2A'}$$

where E_a, R and T have their normal meaning, A' is the temperature amplitude of the applied sinus profile and L stands for $\ln(d\alpha_p/d\alpha_v)$, p and v depict the values on a peak and in a valley, respectively.

4. Results and discussions

4.1. Isothermal measurements

4.1.1. $Mn(Urea)_2Cl_2$

Each of the two decomposition steps of $Mn(Urea)_2Cl_2$ were studied at six different temperatures: for the first step, the temperatures were 145, 160, 165, 175, 185 and 190 °C. For the second decomposition step, we used 210, 225, 235, 240, 245 and 250 °C.

Fig. 1 gives the calculated activation energy E_a as a function of α for the two decomposition steps, calculated from Eq. (2).

As can be seen in the Fig. 1, for both decomposition steps we find a value for E_a which is constant over the entire α-range: 125 kJ/mol for the first step and 170 kJ/mol for the second step. The only exception is near the end of the process, where we see a small but clear deviation from the average vaule for E_a. This is probably due to reading errors in this region of the TGA curve, where it is very flat.

Table 1 gives the values of E_a as a function of α, calculated from Eq. (3). As can be seen, the values are constant over the entire α-region, and the results show the same values as those of Eq. (2).

It is clear that by using relative low temperatures (compared to the critical temperature of 175 °C), the interfering reactions are almost negligible.

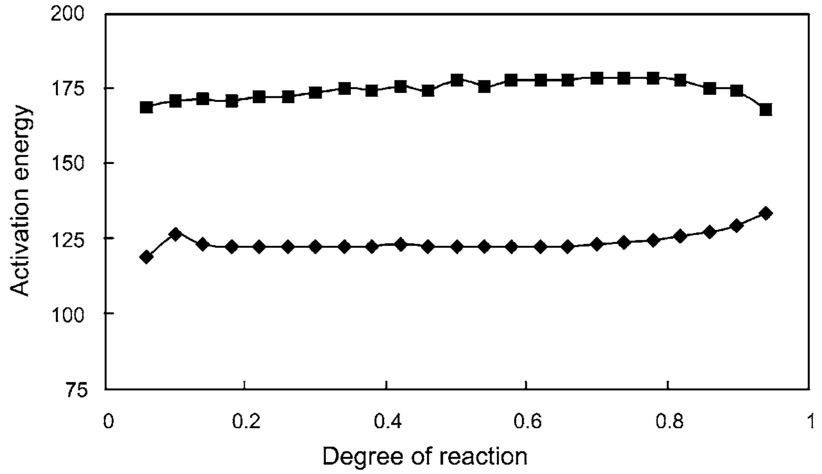

Fig. 1. E_a as a function of α for the first (bottom) and second (top) decomposition step of $Mn(Urea)_2Cl_2$.

Table 1
E_a as a function of α for the two decomposition steps of $Mn(Urea)_2Cl_2$

α	Step 1	Step 2
0.0–1.0	121	175
0.0–0.2	123	171
0.2–0.4	122	174
0.4–0.6	120	176
0.6–0.8	119	178
0.8–1.0	122	173

4.1.2. N-n-propyloxamide

The thermal behaviour of *N*-*n*-propyloxamide was studied at four different temperatures: 115, 120, 125 and 130 °C. Temperatures lower than 115 °C would have resulted in measuring times of more than 24 h and thus in relative large errors due to a very flat TGA curve, for isothermal measurements at temperatures higher than 130 °C a large fraction would have been sublimed before that temperature is reached.

Fig. 2 gives the values of E_a calculated by Eq. (2) as a function of α. In this curve, we see that up to $\alpha = 0.5$ the value for the activation energy stays rather constant around 90 kJ/mol. At higher values of α, the activation energy decreases, but also the correlation coefficient decreases to a rather low value of 0.85–0.9. This is probably due to the flat TGA curve, which causes reading errors in determining the values of t and α.

Calculations using only two or three isothermal measurements show more deviations, which is natural because then we calculate a straight line through a lesser number of points.

The big advantage of isothermal measurements is stability of the results, but the disadvantage is that we need several isothermal measurements at relative low temperatures which take a lot of time.

4.2. Non-isothermal measurements

4.2.1. Linear heating rates

4.2.1.1. $Mn(Urea)_2Cl_2$. For the study under linear heating rates, 14 different values of β between 0.2 and 20 °C/min were used. Fig. 3 shows the mass loss of the first decomposition step as a function of the heating rate, β. For values of β above 0.5 °C/min, we see a decrease in the mass loss due to an increasing amount of non-volatile biuret that is formed.

Fig. 4 shows the plotting of the Kofstad equation for different values of β. In this figure, we see that the slope of the lines changes with increasing heating rates. This is explained by the fact that for higher heating rates (with a larger portion of the decomposition reaction taking place at temperatures above 175 °C) the side reaction becomes more and more important. It is clear that for this process, it is important to study the reaction at low heating rates ($\beta < 0.5$ °C/min) and to concentrate on the begining

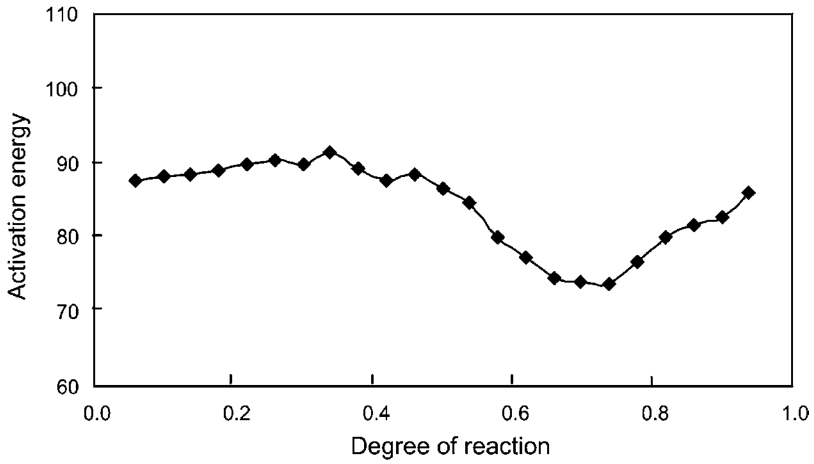

Fig. 2. E_a as a function of α for the sublimation of *N*-*n*-propyloxamide.

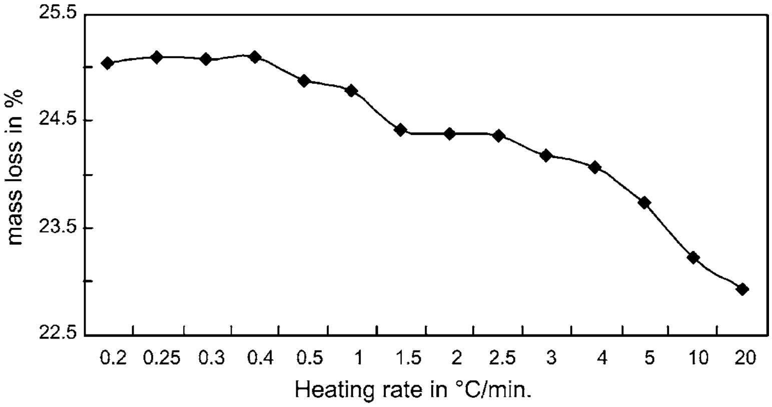

Fig. 3. Mass loss of the first decomposition step as a function of β.

of the reaction because for higher values of β and α a large portion of the decomposition reaction takes place at temperatures above 175 °C, and thus, the calculated activation energy is not that of the pure release of Urea.

Since, for $\beta > 0.5$ °C/min, the side reaction becomes more and more important, we would expect that the value of E_a would increase between 130 kJ/mol (the value for the pure decomposition reaction calculated for very low α and very low β) and 375 kJ/mol (the value for the side reaction) for increasing βs.

Fig. 5 shows the activation energy for the first decomposition reaction of the complex as a function of β, calculated by the Kofstad method for the beginning of the reaction ($\alpha < 0.2$). We see that the experimental values show a minimum. This can be explained by the fact that the Kofstad equation was deduced for a single process and is no longer valid if two processes take place simultaneously.

Table 2 gives an overview of values for the activation energy of the first decomposition step of the complex, calculated for the start of the reaction ($0 \leq \alpha \leq 0.2$) by the different calculation methods based on one thermogravimetric measurement.

Comparing the results of the Kofstad method with those of the Ingraham and Marrier method shows almost identical values. This is an indication that for this process, it is not necessary to represent the

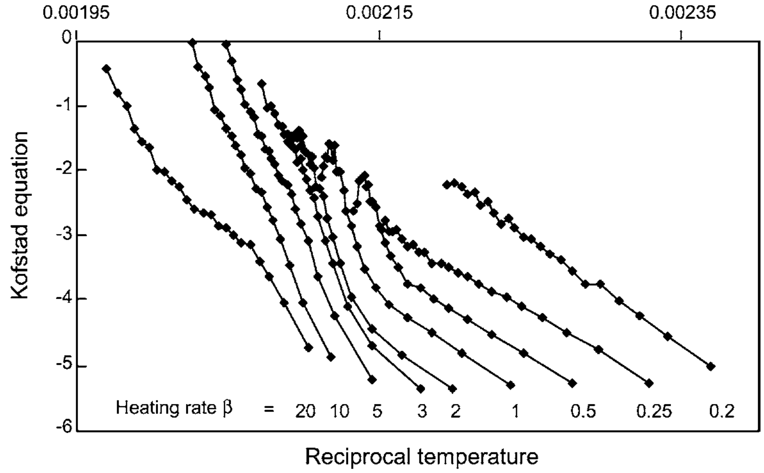

Fig. 4. The Kofstad equation as a function of β.

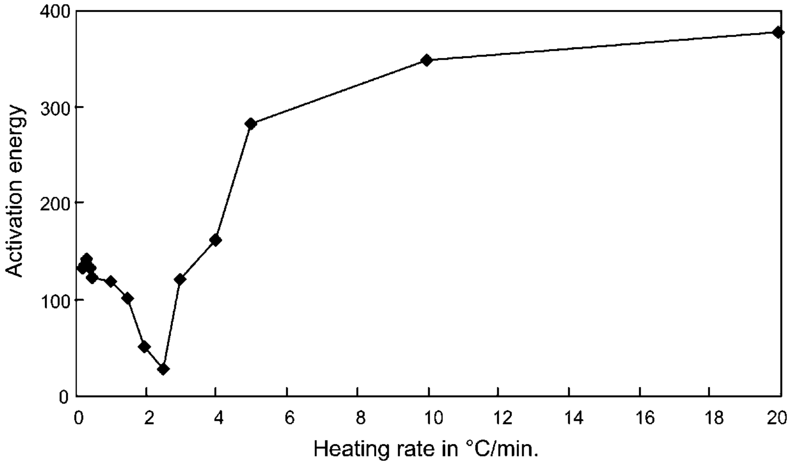

Fig. 5. E_a as a function of β for the first decomposition step.

frequency factor A as a function of temperature as suggested by Ingraham and Marrier. The results of the Freeman and Carroll method show the same trend as those of the previous two methods: an almost constant value for low values of β, a minimum in the intermediate phase and then an increasing value due to the increasing contribution of the side reaction, but the values calculated by the Freeman and Carroll method are lower. We want to remark here that the calculations for this method seem to be sensitive to outliers which influences the accuracy of the slope and, thus, of the activation energy.

For these three methods, we should remember that these are the methods in which the value for E_a is based on only one measurement (one heating rate). Therefor, the dramatic increase of E_a in going from $\beta = 0.2$ to 20 is due to a combination of the poor methods and the influence of the side reaction.

For the general method (using the equation $\ln(d\alpha/dT) = \ln(Af(\alpha)/\beta) - E_a/(RT)$ by plotting $\ln(d\alpha/dT)$ versus $(1/T)$, we see that the resulting values have the same order of magnitude as those found with the three previous methods, except in the intermediate phase of the process, and that we observe the expected evolution of the value of E_a between the value of the first decomposition and that of the side reaction. This can be explained by the fact that the form of $f(\alpha)$ is incorporated in the constant term and thus there is no influence by the fact that the real $f(\alpha)$ is a combination of two reactions.

The two general methods based on several measurements done at different heating rates gave generally the same results, which is normal as they are just mathematical rearrangements. As an example, Fig. 6 gives the activation energy of the first decomposition step as a function of α, calculated from $\ln\beta = \ln[Af(\alpha)/(d\alpha/dT)] - E_a/(RT)$ using all the 14 heating rates between 0.2 and 20 °C/min, while Fig. 7 gives the values obtained using the five low heating rates between 0.2 and 0.5 °C/min.

Table 2
E_a as a function of β for the first decomposition step of $Mn(Urea)_2Cl_2$ for $0.0 \leq \alpha \leq 0.2$

β	Kofstad	Freeman and Carroll	Ingraham and Marrier	$\ln(d\alpha/dT) = f(1/T)$
0.2	131	123	127	133
0.25	135	102	132	120
0.3	141	100	138	117
0.4	131	124	128	131
0.5	122	92	119	121
1.0	119	82	115	129
1.5	100	55	97	145
2.0	51	31	54	196
2.5	27	43	25	234
3.0	120	70	117	272
4.0	161	106	157	318
5.0	282	188	282	387
10.0	348	241	343	375
20.0	377	294	372	290

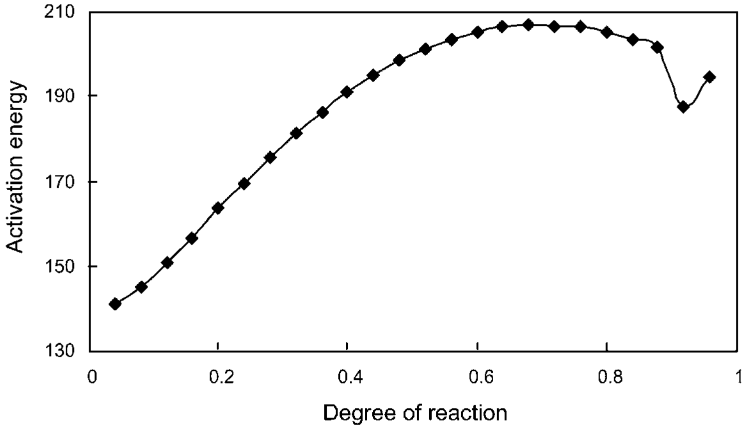

Fig. 6. E_a as a function of α for the first decomposition step ($0.2 \leq \beta \leq 20$ °C/min).

It can be clearly seen that, if we use all values of β, the value of E_a increases due to the known formation of biuret, but if we restrict β to the low values, we find a constant value of 120 kJ/mol up to $\alpha = 0.4$.

So again, we can conclude that it is important to concentrate on the values of E_a calculated for low values of α and β, so that mainly measurements at temperatures lower than 175 °C are considered and the influence of the side reaction (the formation of biuret) is minimized. This is the same conclusion as the one we can draw from the calculations using one non-isothermal measurement.

Calculation of the activation energy for the second decomposition step, using methods based on one measurement, give results with a rather large variation (as expected). Values of E_a, calculated with $\ln \beta = \ln[Af(\alpha)/(\mathrm{d}\alpha/\mathrm{d}T)] - E_a/(RT)$ using 12 heating rates between 0.2 and 5 °C/min, are more stable and give an almost constant value of 170 kJ/mol over the entire α-range. The only deviations are seen at the beginning and at the end of the process, probably due to the fact that in the flattest parts of the (unsmoothed) curve it is more difficult to determine the exact value of the mass. So here too, we can conclude that calculations based on a single run give unreliable results.

We also see that, although the process occurs at higher temperatures, the second decomposition step is less influenced by the side reactions: the temperature

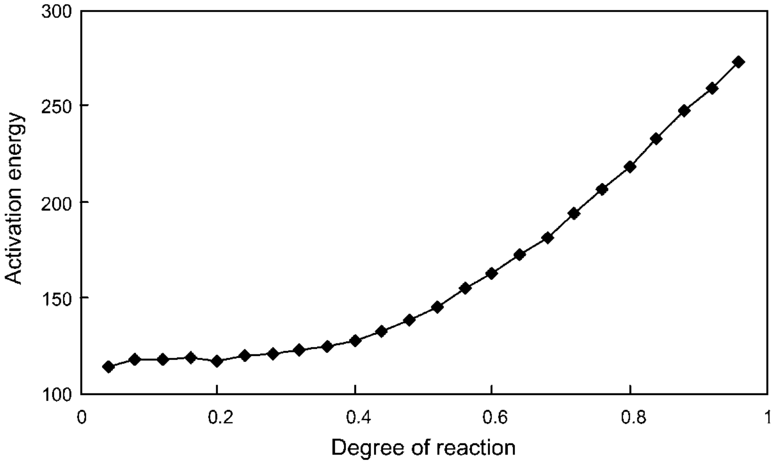

Fig. 7. E_a as a function of α for the first decomposition step ($0.25 \leq \beta \leq 0.5$ °C/min).

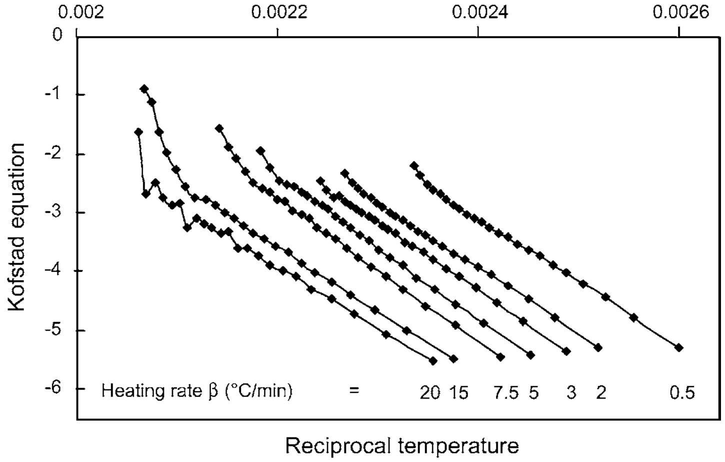

Fig. 8. The Kofstad equation for several values of β.

is too low to decompose the biuret formed in the first step and high enough for the second released Urea to escape before it can be decomposed.

4.2.1.2. N-n-propyloxamide. The sublimation of *N*-*n*-propyloxamide was studied at nine heating rates between 0.5 and 20 °C/min. Fig. 8 shows the results of the Kofstad method for some of these heating rates.

We can clearly see that for low heating rates, we obtain a straight line for almost the entire α-range, while for higher values of β there is a deviation near the end of the process. Just like in the case of the decomposition of the complex, this is caused by a side reaction, in this case the evaporation of the molten compound instead of the sublimation of the solid compound.

If we use only the linear part of the obtained line calculated by the Kofstad method (by limiting the considered α-range so that the correlation coefficient has a minimum value of 0.999), we find the results given in Table 3.

From this table, it can be seen that the activation energy of the sublimation process has a value of 90–100 kJ/mol and gives slightly lower values for higher heating rates. We also see that for higher heating rates, the α-range giving a linear relation decreases because the side reaction (the melting and evaporation) becomes more and more important. This also shows in the DTG curve, where for $\beta > 5$ °C/min the shoulder at the high temperature side due to the side reaction becomes more and more clear.

Fig. 9 gives the activation energy for the sublimation of the amide as a function of the heating rate, calculated from

$$\ln\left(\frac{d\alpha}{dT}\right) = \ln\left(\frac{Af(\alpha)}{\beta}\right) - \frac{E_a}{RT}$$

Since this method seems to be rather sensitive to the influence of side reactions, we restricted the α-range to $0 \leq \alpha \leq 0.2$. In that case, we find the values of 90–95 kJ/mol with a decrease for higher heating rates. We did not use the mehod of Freeman and Carroll nor that of Ingraham and Marrier for the sublimation of *N*-*n*-propyloxamide, because in the study of $Mn(Urea)_2Cl_2$ we already saw that the first one is very sensitive towards the side reactions and that the second one gives values very close to those found with the method of Kofstad.

Table 3
E_a and the used α-range for the sublimation of *N*-*n*-propyloxamide calculated by the Kofstad method

β	α	E_a
0.5	0–0.80	89.0
1	0–0.80	102.3
2	0–0.80	91.4
3	0–0.80	95.3
5	0–0.80	102.7
7.5	0–0.76	102.2
10	0–0.76	93.8
15	0–0.72	91.4
20	0–0.20	84.1

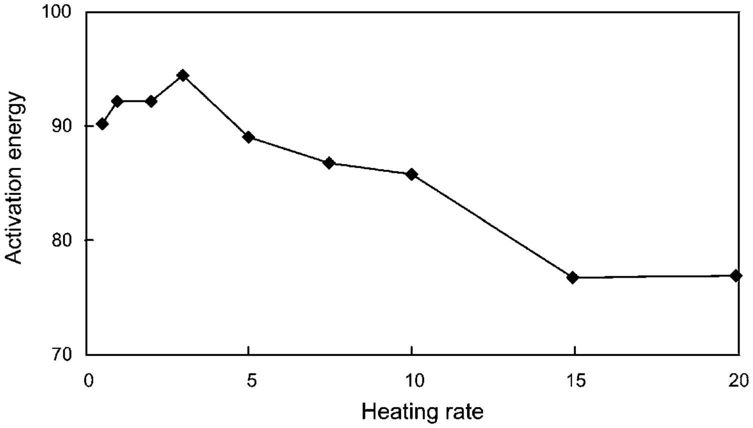

Fig. 9. E_a for the sublimation of *N*-*n*-propyloxamide as a function of α, calculated from $\ln(\mathrm{d}\alpha/\mathrm{d}T) = \ln(Af(\alpha)/\beta) - E_a/(RT)$.

Fig. 10 gives the activation energy for the sublimation of the amide as a function of the degree of conversion, calculated from $\ln\beta = \ln[Af(\alpha)/(\mathrm{d}\alpha/\mathrm{d}T)] - E_a/(RT)$, using nine non-isothermal measurements. We see that the value for E_a decreases slowly for increasing values of β. This can be explained by the fact that the side reaction is melting and the molten compound is evaporating. Since for evaporation no lattice energy needs to be overcome, we expect a lower activation energy for evaporation than for sublimation, and thus a lower total activation energy for the later part of the process, where less sublimation and more evaporation occurs. This process also explains the lowering of the value for E_a for higher heating rates.

4.2.2. Temperature modulated heating rates

4.2.2.1. Mn(Urea)$_2$Cl$_2$. We started our investigations with a temperature profile with an amplitude of 5 °C and a period of 200 s, superimposed on linear heating rates of 0.3, 0.5, 0.8, 1.0, 5.0 and 10.0 °C/min. We noticed that for each of these cases the real obtained amplitude was only 3.6 °C.

Fig. 11 shows E_a as a function of α for both decomposition steps, calculated from the measurement with an underlying linear heating rate of 0.3 °C/min. We see that for each step, three regions can be seen: a high and steep side at the beginning and at the end and a horizontal plateau in between. These high values of E_a at the beginning and at the end can be

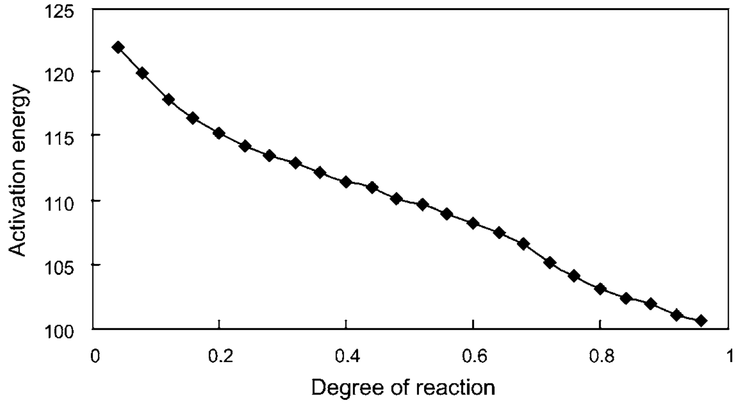

Fig. 10. Activation energy for the sublimation of *N*-*n*-propyloxamide as a function of β, calculated from $\ln\beta = \ln[Af(\alpha)/(\mathrm{d}\alpha/\mathrm{d}T)] - E_a/(RT)$.

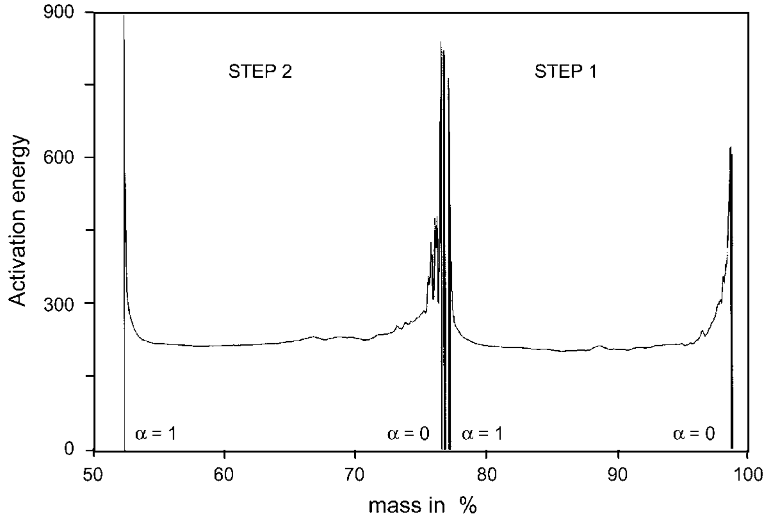

Fig. 11. E_a as a function of α for the decomposition of $Mn(Urea)_2Cl_2$ at 0.3 °C/min.

explained by the fact that $d\alpha_v/dt$ is very low in these regions. It is clear that the calculated values of E_a are not realistic and can not be used.

In Fig. 12 we compare E_a as a function of α for the first decomposition step, calculated from measurements with three different underlying heating rates: 0.3, 1 and 5 °C/min. It can be seen that the higher the heating rate, the smaller the horizontal part and thus the smaller the α-region where meaningful values of E_a can be obtained. For the second decomposition step we see the same effect, but there the value of β can be as high as 10 °C/min before the plateau disappears. This effect is understandable if we take in mind that for this higher heating rates only one or two cylces of the sinus are completed during the whole decomposition process, while it was stated [8] that at least fives cylces should be completed in order to be able to calculate meaningful values of E_a. On top of that, we

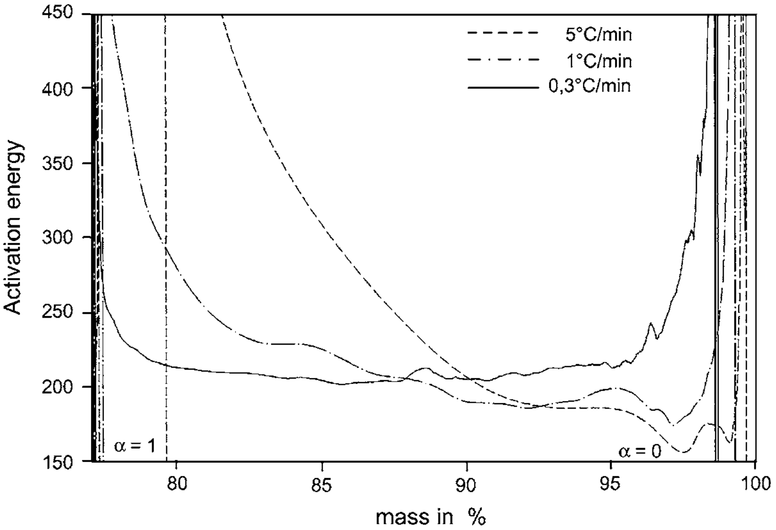

Fig. 12. E_a as a function of α for the first decomposition step of $Mn(Urea)_2Cl_2$ at 0.3, 1 and 5 °C/min.

Table 4
E_a for the two decomposition steps of $Mn(Urea)_2Cl_2$ for different values of β

β	Step 1	Step 2
0.3	202	215
0.5	185	207
0.8	194	202
1.0	186	191
5.0	186	149

must realise that for heating rates of 1 and 5 °C/min, part of the reaction takes places at temperatures above 175 °C so that the side reaction is no longer negligible. Since (as mentioned above), the second decomposition step is less sensitive to the side reaction, the values of E_a for this step are less influenced by the underlying heating rate.

Table 4 gives the calculated values of E_a calculated by modulated TGA (MTGA) with different underlying heating rates. It shows that the values calculated by MTGA are clearly higher than those calculated by normal isothermal and non-isothermal methods. We must remark that in these cases (normal isothermal and non-isothermal methods), we could accept only values calculated for low values of α (even for low βs), while just in this region the MTGA curve of E_a versus α is still in the steep decreasing flank and thus the values can not be used. Therefore, comparison is not evident.

To avoid the problems caused by the side reaction, we decided to study the results of MTGA with an underlying isothermal profile: 165, 175 and 185 °C for the first decomposition step and 225, 235 and 250 °C for the second step, in each case with an amplitude of 5 °C and a period of 200 s. In all these cases, the programmed amplitude of 5 °C was realised, in contrast with the cases of non-isothermal underlying heating profiles, where the actual amplitude was about 3.6 °C for each run.

For the first step, we found 250 kJ/mol at 165 °C and around 220 kJ/mol at 175 and 185 °C. The E_a as a function of α curve at 185 °C shows less noise than the other measurements.

The results for the second step are given in Fig. 13. Here too, like for the first step, the highest temperature gives the lowest value for E_a and shows least noise in the E_a versus α curve. Like for the measurements with non-linear underlying profiles, we find higher values with modulated than with non-modulated measurements.

We also did a few tests with modulated high resolution TGA (Hi-Res TGA), hoping to suppress the side reaction. In Hi-Res TGA, the programmed heating rate is slowed down in order to slow down the mass loss. The resolution factor (RF = 0–8) determines how soon the heating rate is slowed down while the sensitivity ($S = 1$–6) determines how strong the "braking" is. We used heating rates of 0.3, 2 and

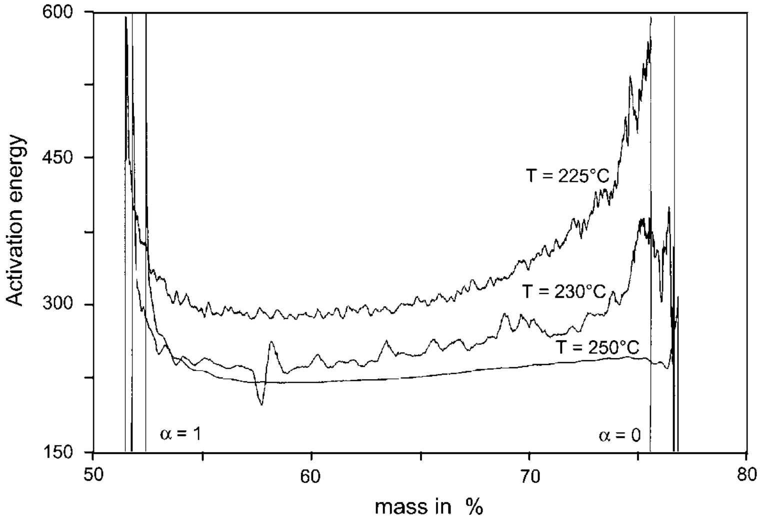

Fig. 13. E_a as a function of α for the second decomposition step of $Mn(Urea)_2Cl_2$.

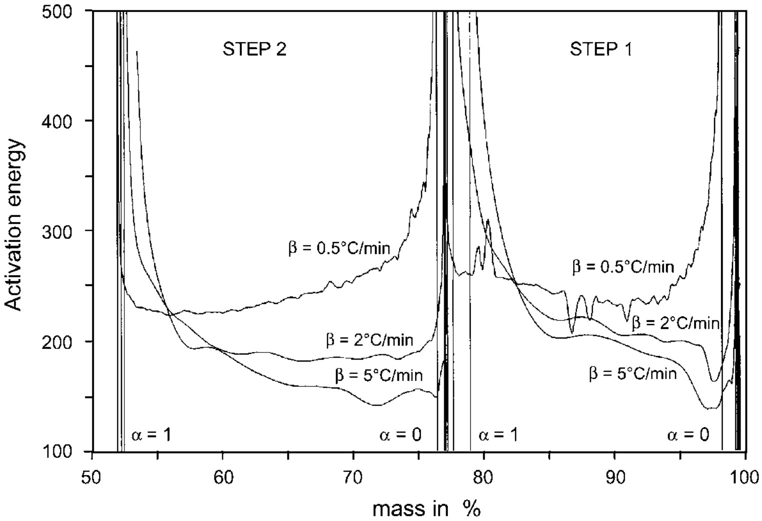

Fig. 14. E_a as a function of α for the two decomposition steps of $Mn(Urea)_2Cl_2$ for $\beta = 0.5$, 2 and 5 °C/min.

5 °C/min, an amplitude of 5 °C and a period of 200 s for the modulation with RF = 6 and $S = 1$. For the heating rates of 0.3 and 5 °C/min, we also did a measurement with RF = 8. We found that, like for the other modulations with non-isothermal underlying profiles, the actual amplitude was only 3.6 instead of the programmed 5 °C.

Fig. 14 shows the activation energy as a function of α for the two decomposition steps measured with three heating rates with RF = 6. For both steps, we find the values of E_a increasing with decreasing heating rate. The heating rates of 2 and 5 °C/min show the profile of the side reactions (in the second half of the reaction). Thus, in these cases, the high resolution procedure was not capable of avoiding these side reactions. For the first step, we find values of E_a that are higher than those found for non-modulated measurements.

Fig. 15 gives the calculated value of E_a as a function of α for the second decomposition step of $Mn(Urea)_2Cl_2$, measured with a heating rate of 0.3 °C/min with

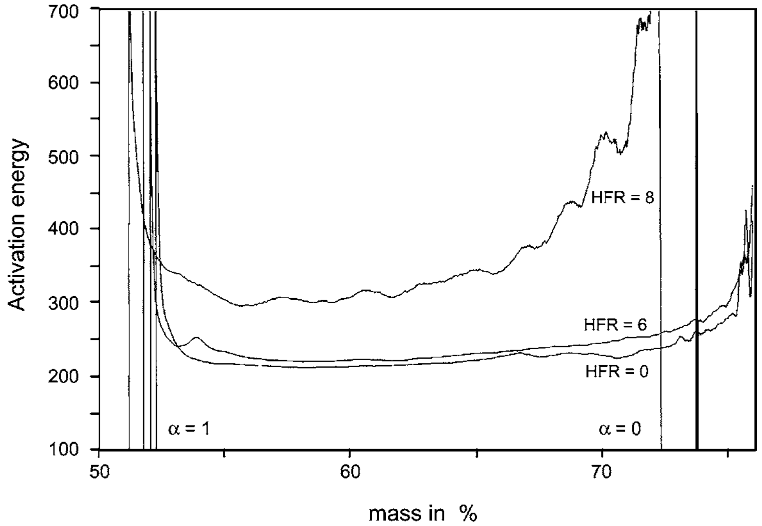

Fig. 15. E_a as a function of α for the second decomposition step of $Mn(Urea)_2Cl_2$ for $\beta = 0.3$ °C/min with RF = 0, 6 and 8.

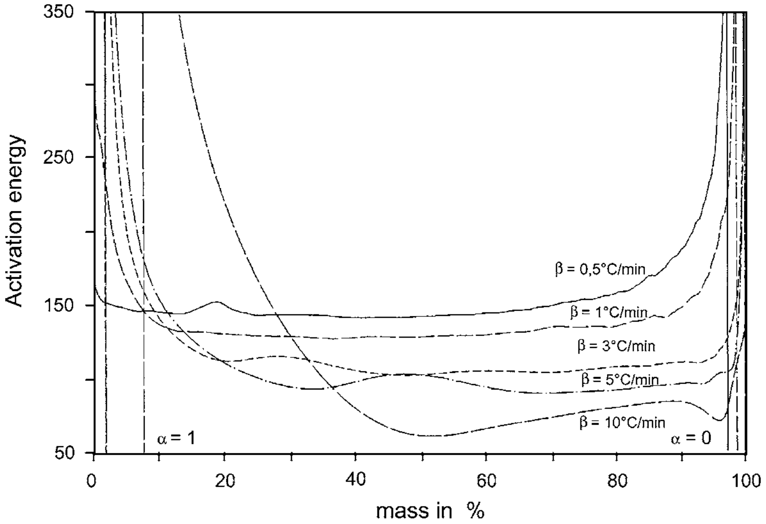

Fig. 16. E_a as a function of α for the sublimation of *N*-*n*-propyloxamide at different heating rates.

RF = 0, 6 and 8 respectively. We can see that E_a increases with increasing RF, an effect that we saw for the first step as well.

4.2.2.2. N-n-propyloxamide. We started with non-isothermal underlying heating profiles of 0.5, 1, 3, 5, 10 and 15 °C/min.

Fig. 16 shows E_a as a function of α for the sublimation of *N*-*n*-propyloxamide, with the different underlying heating profiles. Like in the case of $Mn(Urea)_2Cl_2$ the value of E_a increases with decreasing heating rate. For the highest heating rates (10 and 15 °C/min) we do not obtain a flat plateau, probably because there are not enough periods during the process (two and three respectively).

Next, we used isothermal underlying profiles: 120, 125 and 130 °C. As in the case of $Mn(Urea)_2Cl_2$, the actual amplitude was 5 °C like programmed, while for the non-isothermal underlying profiles it was only 3.6 °C. The results are shown in Fig. 17, from which

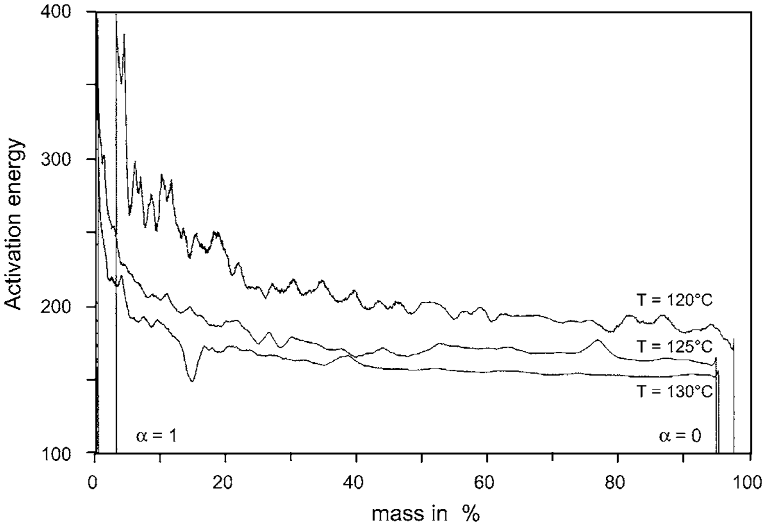

Fig. 17. E_a as a function of α for the sublimation of *N*-*n*-propyloxamide at different temperatures.

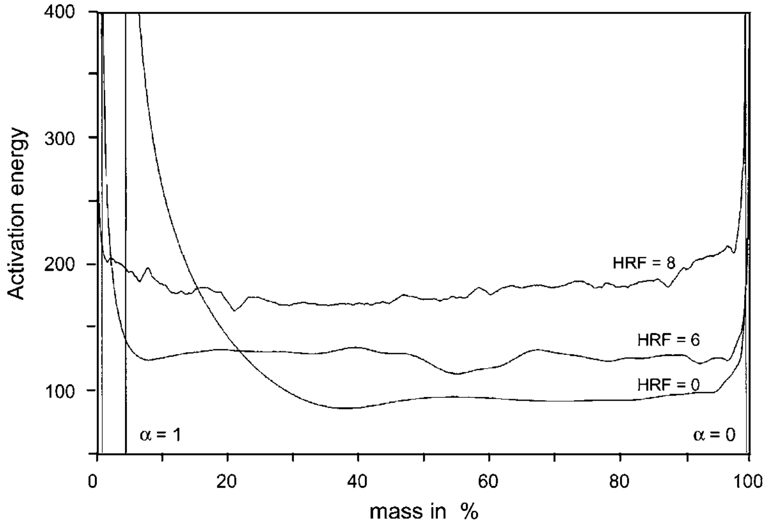

Fig. 18. E_a as a function of α for the sublimation of *N*-*n*-propyloxamide with $\beta = 5$ °C/min and RF $= 0$, 6 and 8.

it is clear that the value of E_a increases with decreasing underlying temperature.

In a final test MTGA was combined with Hi-Res TGA in two runs: heating rate $\beta = 5$ °C/min, amplitude $A = 5$ °C, period $P = 200$ s, sensistivity factor $S = 1$ and high resolution factor (HRF) RF $= 6$ and 8. Fig. 18 shows the results of these two measurements compared with RF $= 0$ (no high resolution) and again we see that E_a increases with increasing RF.

4.2.3. Comparison of the results of the modulated experiments

Table 5 gives an overview of the results of all our modulated experiments. MTGA measurements with non-isothermal underlying heating programme give a E_a versus α curve whose profile quality for the first decomposition step decreases with increasing β, due to the increasing influence of the side reactions. In all other measurements, E_a is influenced by experimental factors: E_a increases with decreasing β. The heating rate should not be too high, to make sure that enough cycles are completed during the process.

For MTGA measurements with isothermal underlying profiles E_a increases with decreasing temperature, as it does with increasing RF for modulated/high resolution combinations.

Decreasing the heating rate, decreasing underlying isothermal temperature and increasing RF all have as result that a certain value of α is attained at a lower temperature. Although some authors recently suggest that E_a could be dependent of temperature, most researchers interprete E_a in the same sense as Arrhenius did: independent of *T*. And so, we feel that there should not be such a clear dependence of the calculated values of E_a as a function of these experimental parameters.

Table 5
Overview of the results of the MTGA measurements

Non-isotherm		
Mn(Urea)$_2$Cl$_2$		
Step 1	$\beta\downarrow$	Better (E_a versus α) profile
Step 2	$\beta\downarrow$	$E_a\uparrow$
N-*n*-propyloxamide	$\beta\downarrow$	$E_a\uparrow$
Isotherm		
Mn(Urea)$_2$Cl$_2$		
Step 1	$T\downarrow$	$E_a\uparrow$
Step 2	$T\downarrow$	$E_a\uparrow$
N-*n*-propyloxamide	$T\downarrow$	$E_a\uparrow$
High resolution		
MnU$_2$Cl$_2$		
Step 1	$\beta\downarrow$, HRF $=$	$E_a\uparrow$
	$\beta =$, HRF $\uparrow$	$E_a\uparrow$
Step 2	$\beta\downarrow$, HRF $=$	$E_a\uparrow$
	$\beta =$, HRF $\uparrow$	$E_a\uparrow$
N-*n*-propyloxamide	$\beta =$, HRF $\uparrow$	$E_a\uparrow$

5. General conclusions

In this article we compared several measuring techniques and calculation methods in order to obtain the activation energy of thermal decomposition reactions. To do so, we compared the sublimation of *N*-*n*-propyloxamide (a process disturbed by the melting and evaporation of the compound only near the end of the reaction and only for high heating rates or high temperatures) with the two-step thermal decomposition of $Mn(Urea)_2Cl_2$ (a process in which the first step is influenced by the decomposition of the released Urea).

Our first conclusion is that it is important to fully understand the process under study before trying to calculate its activation energy. If for instance, we would have calculated the activation energy for the decomposition of $Mn(Urea)_2Cl_2$ based on the Kofstad method for one heating rate (5 °C/min) without knowing the existence of the side reaction, we would have published a value of 282 kJ/mol, while the real value is about 120 kJ/mol.

A second conclusion is that for a single process, the fastest way to calculate E_a is from one non-isothermal measurement, but this is not the most accurate value obtained. Some researchers even insist to completely abandon the single heating rate methods.

If side reactions are known to occur, it is necessary to search for experimental circumstances that minimise these side reactions. In many case they can be avoided by isothermal measurements at relatively low temperatures. A very reliable value of E_a versus α can be calclulated by using enough temperatures (at least four). However, this increases the measurement time.

This inconvenience (long measuring times) can be solved by MTGA, but we showed that the accuracy is limited, since we found a temperature dependence which is in contradiction with theory. Thus, the calculation method of E_a from MTGA measurements will need some revision.

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