

## **KINETIC ANALYSIS OF LIQUID-PHASE DEPOLYMERIZATION OF TRIOXANE FROM PROGRAMMED TEMPERATURE DATA**

### **II. Sequential kinetic analysis**

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A sequential kinetic discrimination of potential kinetic models for non-isothermal linear programmed temperature data on the depolymerization of trioxane in a homogeneous liquid phase has been discussed.

The influence of the initial concentration on the kinetic curves has been used as an experimental confirmation of the first-order influence of the concentration on the model.

Kinetic analysis at constant temperature and conversion permits separation of the effects of concentration and temperature on the kinetic analysis at different levels of the variables.

It is provided via non-isothermal kinetic data on the depolymerization of trioxane that non-isothermal experiments allow a systematic approach to the kinetic behaviour in a wide range of the variables temperature and concentration, leading to maximum knowledge of the reaction model through minimum experimental effort.

A kinetic investigation consists mainly in model discrimination and parameter estimation; the kinetic studies are usually carried out under isothermal conditions, the influence of the temperature and concentration in the kinetic model being analysed in different experiments.

Many papers have reported isothermal kinetic studies of different reactions, where an initial function of the temperature ( $T$ ) and concentration ( $C$ ) is taken for the reaction rate ( $r$ ):

$$r = F_0(T, C) \quad (1)$$

From a mathematical point of view, many reactions are described by separable variable models, where the function of temperature and concentration can be

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separated as the product of a function of temperature and a function of concentration:

$$r = f_T(T) \cdot f_C(C) \quad (2)$$

The Arrhenius law has usually been taken as describing the influence of the temperature on the reaction rate:

$$f_T(T) = k = A \cdot \exp(-E/RT) \quad (3)$$

The effect of the concentration rate is generally described by a power expression, taking:

$$F_C(C) = C^n \quad (4)$$

where  $n$  is the reaction order, usually with the value 0, 1 or 2.

In these cases the reaction rate can be described by an expression:

$$r = A \cdot \exp(-E/RT) \cdot C^n \quad (5)$$

where  $n$  describes the influence of the concentration on the reaction rate and  $E$  the influence of the temperature.

The application of a programmed temperature method to the kinetic modelling of chemical reactions in a liquid phase has been explained [2, 3] using a linear rise of temperature during the reaction. The application of the integral method of data analysis has been described in a previous work for the kinetic modelling of the depolymerization of trioxane [4]. In the present work, different heating rates have been used as the variable to separate the effects of concentration and temperature on the modelling of the depolymerization of trioxane.

This sequential method seems to be very useful to cover the possible changes in the activation energy or concentration influence during the experiment, because one of the major problems in non-isothermal kinetic analysis is that only one experiment covers a wide range of variables. While an isothermal experiment depends only on the influence of the concentration change during the reaction, a non-isothermal experiment depends on the concentration and temperature changes, and the observed results can be due to a modification of the mechanism of the reaction in the range of temperature employed.

If the programmed temperature method is used in the investigation of reaction kinetics in a liquid phase, only the difference between the correlation coefficients (which can be small) decides the selected kinetic model, and the data are often too scanty or not sufficiently precise to distinguish such a difference. In these cases, the sequential model discrimination can be followed by using the initial concentration  $C_0$  and the heating rate  $\beta$  as variables to separate the effects of the temperature and

concentration on the kinetic model, as has been explained for thermal decomposition reactions [5, 6].

Successful results have been obtained for the kinetic interpretation at constant temperatures and constant conversions of reactions taking place at different heating rates.

These results show the experimental feasibility of the method, which is limited to simple kinetic models of separable variables and seems to be very useful for a critical evaluation of the kinetic results obtained from a fitting to one linear temperature rise experiment, and for the study of the possible changes in the kinetic mechanism with the temperature or the concentration.

### Experimental method

A simple experimental set-up to perform reactions in the liquid phase under linear temperature rise was described in part I of this work.

Iodometric determination of free formaldehyde [7] was used to obtain the conversion vs. time/temperature curves for the studied reaction. An experimental error of less than 1% was determined statistically for the titration.

1.5%, 3% and 4.5% solutions of trioxane (Merck) in 4 M sulphuric acid were used in the kinetic determination.

### Results and interpretation

#### *Initial concentration as variable*

The kinetic results expressed as trioxane conversion vs. temperature are shown in Fig. 1 for different initial concentrations of trioxane, with  $C_0 = 1.5\%$ , 3% and 4.5%, and  $\beta = 2$  deg/min.

The sequential kinetic analysis starts with the simple observation that the kinetic conversion vs. temperature curves are superimposed for the different initial concentrations, taking into account that the curves can be characterized for potential kinetic models by the equation:

$$f(x) = \frac{A}{\beta C_0^{1-n} \int_{T_0}^T \exp(-E/RT) dT} \quad (6)$$

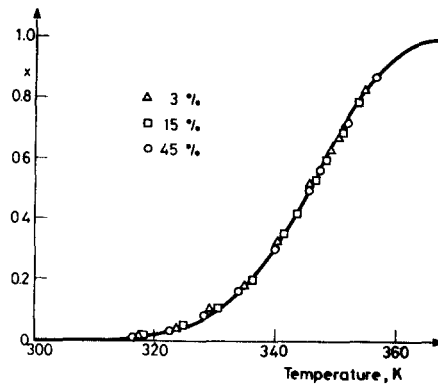
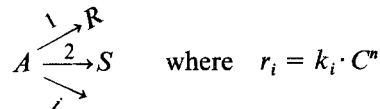


Fig. 1 Conversion of trioxane vs. temperature for different initial concentrations.  $\beta = 2$  deg/min,  $C_0 = 1.5, 3.0$  and  $4.5\%$

The fact that the kinetic curves are independent of the initial trioxane concentration leads to the conclusion that a potential kinetic model of first order ( $n = 1$ ) may describe the kinetic behaviour of the reaction rate.

The experimentation under programmed temperature conditions at different initial concentrations has as main advantage that the reaction order is not dependent on the function which describes the influence of the temperature on the reaction rate, and if parallel reactions of the same order are taking place, the influence of the concentration on the kinetic model can be evaluated:



which after developing (4):

$$f(x) = \frac{1}{C_0^{1-n}} \sum_{i=0}^i A_i \int_{T_0}^T \exp(-E/RT) dt \quad (7)$$

where  $i$  means the parallel reaction and  $n$  must be the same order for all parallel reactions.

In these cases the complex influence of the temperature on the kinetic model can be avoided through experiments involving the same temperature programme and different initial concentrations.

A parallel reaction scheme shows the same superimposed curves when the initial concentration is taken as variable and the reaction is of first order.

Two different cases can be distinguished if the kinetic curves are not superimposed, when a separable variable model can be applied to describe the reaction. This is the case for a potential kinetic model of order 0 or 2, or when a non-separable variable model must be used to describe the reaction.

In the first case, if points are taken at the same temperature from kinetic curves for different initial concentrations, a linear fitting of  $f(x)$  and  $1/C_0^{1-n}$  must be obtained for the correct reaction order.

An indication of the necessity of non-separable variable models can be obtained when the best reaction order is a fractional one.

#### *Heating rate as variable*

The kinetic results expressed as trioxane conversion vs. temperature are shown in Fig. 2 for different heating rates, with  $\beta = 0.50, 0.75, 1$  and  $2$  deg/min and  $C_0 = 3\%$ .

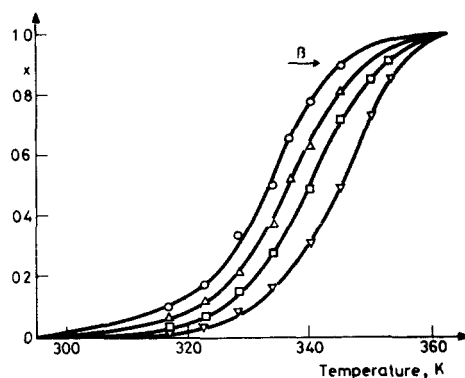


Fig. 2 Conversion of trioxane vs. temperature for different heating rates.  $C_0 = 3\%$ .  $\beta = 0.5, 0.75, 1$  and  $2$  deg/min

#### *Analysis at constant temperature*

For simple or parallel reactions of the same order and following the Arrhenius law:

$$f(x) = \frac{AT_0}{\beta C_0^{1-n}} I(Ar, y) \quad (8)$$

where  $I(Ar, y)$  is the integral function of the non-dimensional temperature,  $y = T/T_0$ , and  $Ar = E/RT_0$ , the Arrhenius number.

In the kinetic curves for the same initial concentration and different heating rates,

$x$  values for the same temperature can be taken as shown in Table 1, and different reaction orders can be checked by taking  $f(x)$  functions and fitting these data to  $1/\beta$  by linear regression as shown in Table 2. The best fitting of the data is shown in Fig. 3 for different temperatures ( $y$ ), obviously for the first-order model.

The slopes of these fittings correspond to  $AT_0 \cdot I(Ar, y)$  and different Arrhenius numbers must now be checked to obtain the preexponential factor and the

**Table 1** Conversion data at different heating rates for the same temperature

$y$	$x$	$\beta$
1.1	10.5	0.5
	6.0	0.75
	3.0	1.0
	1.0	2.0
1.12	17.5	0.5
	12.0	0.75
	7.0	1.0
	3.5	2.0
1.14	33.5	0.5
	21.5	0.75
	15	1.0
	8.5	2.0
1.16	50.0	0.5
	37.5	0.75
	28	1.0
	16.5	2.0
1.18	77.5	0.5
	62.5	0.75
	49	1.0
	31	2.0

**Table 2** Correlation parameters for different reaction orders

$y$	$n=0$	$n=1$	$n=2$
	$r^2$	$r^2$	$r^2$
1.10	0.9828	0.9904 <sup>a</sup>	0.9780
1.12	0.9843	0.9942	0.9829
1.14	0.9934	0.9953	0.9733
1.16	0.9935	0.9969	0.9887
1.18	0.9815	0.9951	0.9578

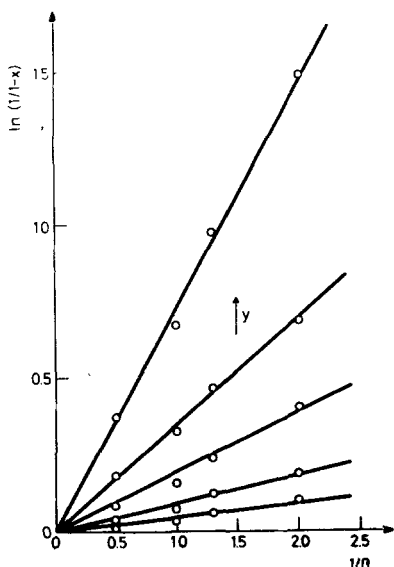


Fig. 3  $\ln 1/(1-x)$  vs.  $1/\beta$  at constant temperatures.  $y = 1.10, 1.12, 1.14, 1.16$  and  $1.18$

Table 3 Correlation parameters for different Arrhenius numbers

$Ar$	Slope	Or. ord.	$r^2$
10	$5.31 \cdot 10^4$	$-4.07 \cdot 10^{-1}$	0.9011
20	$3.34 \cdot 10^8$	$-1.90 \cdot 10^{-1}$	0.9439
30	$2.02 \cdot 10^{12}$	$-1.16 \cdot 10^{-2}$	0.9729
40	$1.18 \cdot 10^{16}$	$-1.39 \cdot 10^{-3}$	0.9894
50	$6.71 \cdot 10^{19}$	$4.28 \cdot 10^{-2}$	0.990

activation energy. Different methods can be applied to solve the integral variable. A numerical integration method such as Simpson's rule or the trapezoidal rule leads to exact values of the integral variable. With this method, a linear fitting of the slopes to the integral variable at different Arrhenius numbers between 10 and 50 is shown in Table 3. The best fitting of the data lies between Arrhenius numbers of 30 and 50, leading to a best Arrhenius number of 41, as shown in Fig. 4, with the following correlation parameters:

$$Ar = 41, \quad A \cdot T_0 = 2.807 \cdot 10^{16} \quad \text{and} \quad r^2 = 0.991$$

From the substitutions  $T_0 = 288$  K and  $Ar = 41$ , we have  $A = 9.42 \cdot 10^{13}$ .

Approximative methods can be used in the integration. Lee and Beck [8] suggest

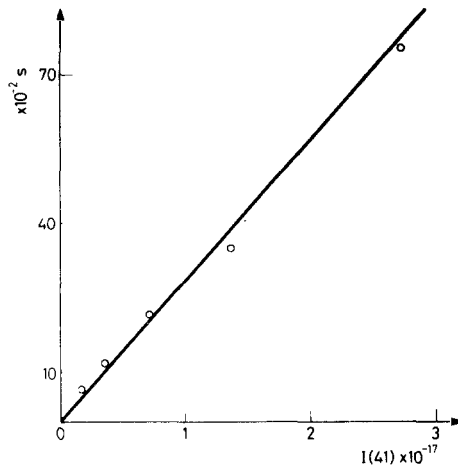


Fig. 4 Slope vs.  $I(Ar, y)$  for  $Ar = 41$

the equation:

$$\frac{A}{\beta} \int_{T_0}^T \exp(-E/RT) dT \cong \frac{A}{\beta} \frac{\left(\frac{RT^2}{E}\right) \exp(-E/RT)}{\left(1 + \frac{2RT}{E}\right)} - \frac{\left(\frac{RT_0^2}{E}\right) \exp(-E/RT_0)}{\left(1 + \frac{2RT_0}{E}\right)} \quad (9)$$

and after normalization

$$I \cong \frac{\frac{y^2}{Ar} \exp(-Ar/y)}{\left(1 + \frac{2y}{Ar}\right)} - \frac{\frac{1}{Ar} \exp(-Ar)}{\left(1 + \frac{2}{Ar}\right)} \quad (10)$$

or the well-known Coats and Redfern approximation [9], where:

$$I \cong \frac{y^2}{Ar} \left(1 - \frac{2y}{Ar}\right) \exp(-Ar/y) - \frac{1}{Ar} \left(1 - \frac{2}{Ar}\right) \exp(-Ar) \quad (11)$$

In the cases where

$$\frac{\frac{1}{Ar} \exp(-Ar)}{\left(1 + \frac{2}{Ar}\right)} \ll \frac{\frac{y^2}{Ar} \exp(-Ar/y)}{\left(1 + \frac{2y}{Ar}\right)}$$



or  $\frac{1}{Ar} \left(1 - \frac{2}{Ar}\right) \exp(-Ar) \ll \frac{y^2}{Ar} \left(1 - \frac{2y}{Ar}\right) \exp(-Ar/y)$ :

$$I \cong \frac{\frac{y^2}{Ar} \exp(-Ar/y)}{\left(1 + \frac{2y}{Ar}\right)} \quad (12)$$

and

$$I \cong \frac{y^2}{Ar} \left(1 - \frac{2y}{Ar}\right) \exp(-Ar/y) \quad (13)$$

In the cases where  $\frac{2y}{Ar} \ll 1$ :

$$I \cong \frac{y^2}{Ar} \exp(-Ar/y) \quad (14)$$

These approximations depend very much on the  $y$  values and Arrhenius numbers, but Eq. (14) can be used as a first approximation because it has the important advantage that it is easily proved in graphical form.

Considering Eq. (14):

$$s \cong AT_0 \frac{y^2}{Ar} \exp(-Ar/y) \quad (15)$$

which can be plotted in a linear form taking:

$$\ln \frac{s}{y^2} = \ln \frac{AT_0}{Ar} - \frac{Ar}{y} \quad (16)$$

As shown in Fig. 5, after linear regression  $Ar = 39.5$ . A consideration of the approximation of the integral variable leads to errors less than 5%.

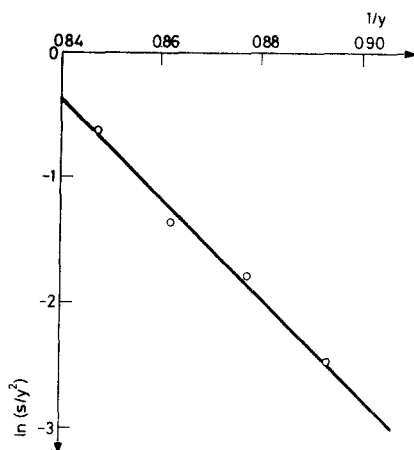
#### *Analysis at constant conversion*

In the kinetic curves for the same initial concentration and different heating rates,  $y$  values for the same  $x$  can be taken as shown in Table 4, and the approximate expression for the integral variable can be checked by taking:

$$f(x) \cong \frac{AT_0}{\beta C_0^{1-n}} \frac{y^2}{Ar} \exp(-Ar/y) \quad (17)$$

where:

$$\ln \frac{\beta}{y^2} = \ln \frac{AT_0}{f(x) C_0^{1-n} Ar} - \frac{Ar}{y} \quad (18)$$

Fig. 5  $\ln s/y^2$  vs.  $1/y$ **Table 4** "y" values for the same conversion at different heating rates

$x$	$y$	$\beta$
0.10	1.098	0.5
	1.115	0.75
	1.128	1.0
	1.144	2.0
0.20	1.126	0.5
	1.136	0.75
	1.149	1.0
	1.166	2.0
0.40	1.149	0.5
	1.160	0.75
	1.172	1.0
	1.190	2.0
0.60	1.168	0.5
	1.177	0.75
	1.188	1.0
	1.208	2.0
0.80	1.184	0.5
	1.194	0.75
	1.209	1.0
	1.229	2.0

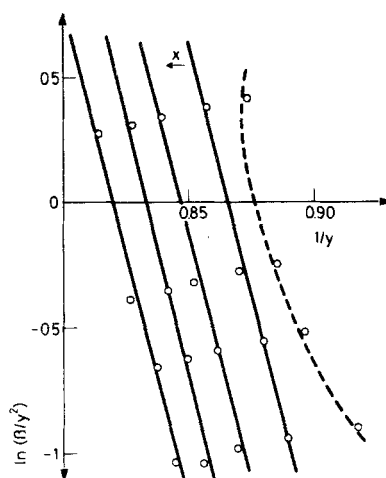


Fig. 6  $\ln \beta/y^2$  vs.  $1/y$

Table 5 Correlation parameters for  $\ln \beta/y^2$  vs.  $1/y$  at different conversions

$x$	$-Ar$	$r^2$
0.10	-34.7	0.96
0.20	-41.7	0.98
0.40	-43.0	0.99
0.60	-45.3	0.99
0.80	-40.7	0.98

A linear fitting of the data is shown in Fig. 6 for the different conversions.

An Arrhenius number of  $Ar = 41$  can be taken as the main value, and the influence of the temperature at different conversions can be described by this value, as shown in Table 5.

## Conclusions

The sequential kinetic method of data analysis from programmed temperature data has been used for determination of the kinetic model of depolymerization of trioxane in a homogeneous liquid phase. Similar values of the kinetic parameters are obtained from isothermal data [10].

With the initial concentration and the heating rate as variables, an extensive

kinetic analysis can be performed by detecting the possible changes in the influence of the concentration or the temperature on the reaction rate from programmed temperature data.

This method may solve some of the usual problems encountered in kinetic analysis with non-isothermal data, relating to the complex influence of the concentration or temperature on the kinetic model.

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**Zusammenfassung** — Eine sequentielle kinetische Unterscheidung potentieller kinetischer Modelle für die nicht-isotherme, linear temperaturprogrammierte Depolymerisation von Trioxan in homogener flüssiger Phase wird diskutiert. Der Einfluß der Ausgangskonzentration auf die kinetischen Kurven wurde als experimentelle Bestätigung dafür angesehen, daß die Konzentration auf das Modell nach erster Ordnung einwirkt. Die kinetische Analyse bei konstanter Temperatur und Konversion ermöglicht eine Trennung des Einflusses der Konzentration und Temperatur auf die kinetische Analyse bei unterschiedlichen Werten dieser Variablen. In der vorliegenden Arbeit wurde anhand von nicht-isothermen kinetischen Daten für die Depolymerisation von Trioxan gezeigt, daß nicht-isotherme Experimente eine systematische Näherung an das kinetische Verhalten in einem weiten Bereich der Variablen Temperatur und Konzentration erlauben und zu einem Maximum an Erkenntnissen über das Reaktionsmodell bei einem Minimum an experimentellen Aufwand führen.

**Резюме** — Обсуждено последовательное кинетическое различие потенциальных кинетических моделей для неизотермического линейно-программированного нагрева гомогенной жидко-фазной реакции деполимеризации триоксана. Влияние начальной концентрации на кинетические кривые было использовано в качестве экспериментального подтверждения первого порядка влияния концентрации на модельную реакцию. Кинетический анализ при постоянной температуре и степень превращения позволили разделить влияние концентрации и температуры на кинетический анализ при различных степенях этих переменных. На примере неизотермических кинетических данных реакции деполимеризации триоксана доказано, что неизотермические эксперименты позволяют осуществить систематический подход к кинетическому поведению в широкой области переменных, температуры и концентрации, давая тем самым максимум знаний о модельной реакции при минимуме экспериментальных попыток.