Journal of Thermal Analysis, Vol. 32 (1987) 997–1004

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

I. Integral kinetic analysis

M. I. Ortiz and *A. Irabien*

DPTO. DE QUIMICA TÉCNICA, FACULTAD DE CIENCIAS,
UNIVERSIDAD DEL PAIS VASCO, APDO. 644, BILBAO, SPAIN

(Received September 16, 1985)

An experimental method for the determination of kinetic data for liquid-phase reactions under linear rise of temperature is explained for the depolymerization of trioxane. Integral kinetic analysis of the data is performed in order to determine the kinetic model and the kinetic parameters. Experiments have been carried out at different heating rates between 0.5 and 2 deg/min, leading to similar kinetic parameters. The obtained results are in agreement with the kinetic model and parameters obtained from isothermal kinetic analysis. The programmed-temperature method seems to be a useful tool for a quick determination of kinetic models, avoiding experimental work.

Most chemical reaction analysis for reactions taking place in a homogeneous liquid phase has been carried out under isothermal conditions [1–3] and little progress has been achieved in the application of non-isothermal methods (usually employed in the study of gas-solid decomposition reactions [4–6]) to liquid-phase reactions [7–10].

A simple method for the kinetic analysis of liquid-phase reactions from programmed-temperature data has recently been published [11, 12], including the theoretical basis and the simulation results for the kinetic analysis of potential laws.

The programmed-temperature method for the kinetic analysis of liquid-phase reactions is applied in this work to the experimental determination of the kinetic model and parameters in the depolymerization of trioxane.

For liquid-phase reactions where the concentration measurements are carried out discontinuously, small amounts of the reaction mixture being taken at known intervals of time and chemical analysis of the mixture composition being performed, the thermoanalytical method (TA) allows experimental determination

Correspondence should be addressed to A. Irabien.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

of the thermoanalytical curves during the progress of the reaction with the time/temperature relation under programmed-temperature variation.

A simple experimental system has been developed for liquid-phase reactions with programmed temperature. The kinetic modelling of the reaction was performed from the thermoanalytical data, with the Arrhenius number $\mathrm{Ar} = E_a/RT_0$ and the reaction order n as parameters.

The method is particularly suitable for the rapid and simple kinetic modelling of industrial liquid-phase reactions, because chemical reaction engineering is not usually concerned with the mechanisms of the reactions taking place in the manufacturing process. The scope of these kinetic studies is the development of kinetic models which can describe the chemical reaction behaviour in the range of variables of the industrial process. It is not very important for this objective if the kinetic model has some mechanistic implications, as nearly all the kinetic models for industrial reactions are empirically developed and calculation of the kinetic parameters from molecular theories is not possible.

The main point of this kinetic work is the evaluation of useful kinetic parameters to be introduced in the analysis and modelling of chemical reactors, so that much experimental effort can be avoided by applying this programmed-temperature method to the modelling of chemical reactions.

The comparison of our results for the depolymerization of trioxane with the results obtained from isothermal kinetic methods [13] shows that the same information on the reaction modelling can be obtained with a minimum of experimental effort.

Experimental method

A system with programmed temperature has been developed. A 250 cm^3 flask fitted with a magnetic stirrer, a reflux condenser, a thermometer and an outlet for samples introduced into a water-bath has been used. The thermometer is placed into the flask in contact with the reaction mixture. No difference has been found in the temperature in the reaction mixture. The thermometer is connected to a heating system which can be programmed at different temperature gradients through heating of the water-bath.

This installation allows control of the temperature programme of the reaction mixture.

Samples are taken from the flask with a syringe at known temperature/time values.

The reaction is stopped by neutralization of the samples, which are weighed to find the exact amount. Iodometric analysis of formaldehyde [14] is carried out to determine the conversion of the depolymerization reaction.

Trioxane (Merck) was used to determine the rate of depolymerization. This is stable in neutral and alkaline solutions, but is depolymerized by strong acids; thus, a 4 *M* sulphuric acid concentration was used in the reaction. Acidified 3% trioxane solutions were used in the kinetic studies to be compared with the isothermal results carried out at this concentration [13].

Results and interpretation

Results are shown in Fig. 1, as trioxane conversion *vs.* temperature for different heating rates: $\beta = 0.5, 0.75, 1$ and 2 deg/min.

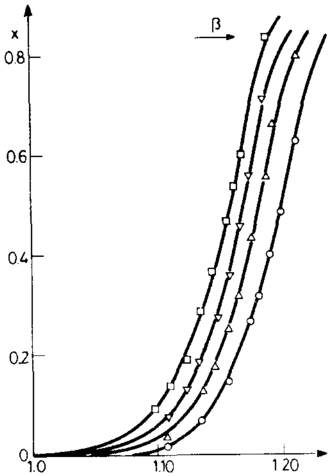

Fig. 1 Conversion of trioxane *vs.* non dimensional temperature for $\beta = 0.5, 0.75, 1$ and 2 deg/min

The reaction rate can be expressed by:

$$r = F(k, C) \tag{1}$$

For experiments taking place under non-isothermal linear temperature change, considering a separable-variable kinetic expression and the Arrhenius law for the influence of the temperature on the kinetic constant:

$$\int_{0}^{C} \frac{\mathrm{d}C}{g(C)} = \int_{T_0}^{T} A \exp(-E/RT) \frac{1}{\beta} \mathrm{d}T \tag{2}$$

If a potential kinetic model is assumed, $g(C) = C^n$, and the concentration and temperature are expressed in a non-dimensional way:

$$f(x) = \frac{AT_0}{\beta C_0^{1-n}} \int_1^y \exp(-Ar/y)\,\mathrm{d}y \tag{3}$$

where x is the conversion, y the non-dimensional temperature T/T_0, taking $T_0 = 288$ K, $Ar = E/RT_0$ the Arrhenius number and $f(x)$ is the integrated function of the conversion, which depends on the potential order, being $f(x) = x$ for $n=0$, $f(x) = \ln\frac{1}{1-x}$ for $n=1$ and $f(x) = x/(1-x)$ for $n=2$.

In the model evaluation, the integral expression $\int_1^y \exp(-\mathrm{Ar}/y)\,\mathrm{d}y$ has been calculated in the range of experimental results $1 \leqslant y \leqslant 1.3$ for different values of the Arrhenius number between 10 and 50, at intervals of 10. These results have been normalized, taking

$$I = \frac{\int_1^y \exp(-\mathrm{Ar}/y)\,\mathrm{d}y}{\exp(-\mathrm{Ar})}$$

For the correct reaction order and Arrhenius number, the experimental x, y curves must be described by a linear relation between the conversion function corresponding to the kinetic order $f(x)$ and the integral function of the temperature I:

$$f(x) = s \cdot I(\mathrm{Ar}, y) \tag{4}$$

where

$$s = \frac{AT_0 \exp(-\mathrm{Ar})}{\beta C_0^{1-n}}$$

This fitting must give the kinetic model (reaction order) and kinetic parameters (A and E).

Kinetic functions corresponding to reaction orders of 0, 1 and 2 have been fitted by linear regression to the integral function for different Arrhenius numbers, as shown in Fig. 2.

From this Figure it can be deduced that the best correlation coefficients correspond to the first-order kinetic model and the best value of the Arrhenius number lies between 35 and 45.

The parameters for the linear fitting from Ar = 35 to Ar = 45 are shown in Tables 1–4.

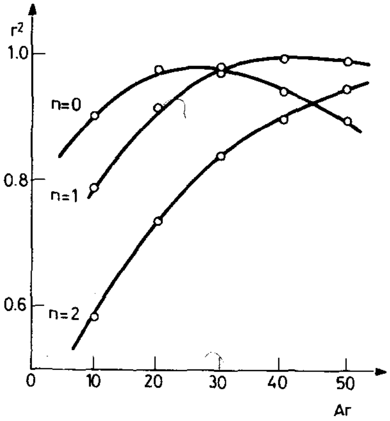

Fig. 2 Correlation coefficients of $f(x)$ *vs.* I for different Arrhenius numbers of β = 0.75 deg/min

Table 1 Parameters for the linear correlation at different Arrhenius numbers, β = 0.5 deg/min

Ar	s	0.0	r^2
35	$1.93 \cdot 10^{-1}$	$-5.32 \cdot 10^{-2}$	0.9955
37	$1.48 \cdot 10^{-1}$	$-3.27 \cdot 10^{-2}$	0.9978
39	$1.13 \cdot 10^{-1}$	$-1.30 \cdot 10^{-2}$	0.9990
41	$8.58 \cdot 10^{-2}$	$5.7 \cdot 10^{-3}$	0.9994
43	$6.51 \cdot 10^{-2}$	$2.35 \cdot 10^{-2}$	0.9990
45	$4.94 \cdot 10^{-2}$	$4.04 \cdot 10^{-2}$	0.9980

Table 2 Parameters for the linear correlation at different Arrhenius number, β = 0.75 deg/min

Ar	s	0.0	r^2
35	$1.42 \cdot 10^{-2}$	$-9.88 \cdot 10^{-2}$	0.989
37	$1.21 \cdot 10^{-2}$	$-7.63 \cdot 10^{-2}$	0.9924
39	$8.33 \cdot 10^{-2}$	$-5.5 \cdot 10^{-2}$	0.9947
41	$6.98 \cdot 10^{-2}$	$3.47 \cdot 10^{-3}$	0.9969
43	$4.36 \cdot 10^{-2}$	$1.56 \cdot 10^{-2}$	0.9966
45	$2.15 \cdot 10^{-2}$	$2.6 \cdot 10^{-2}$	0.9960

Table 3 Parameters for the linear correlation at different Arrhenius numbers, $\beta = 1$ deg/min

Ar	s	0.0	R^2
34	$1.10 \cdot 10^{-1}$	$-4.8 \cdot 10^{-2}$	0.9812
36	$8.17 \cdot 10^{-2}$	$-2.76 \cdot 10^{-2}$	0.9823
38	$6.04 \cdot 10^{-2}$	$-8.4 \cdot 10^{-3}$	0.9845
41	$3.81 \cdot 10^{-2}$	$1.82 \cdot 10^{-2}$	0.9899
43	$2.80 \cdot 10^{-2}$	$3.45 \cdot 10^{-2}$	0.9758
45	$1.51 \cdot 10^{-2}$	$4.99 \cdot 10^{-2}$	0.9712

Table 4 Parameters for the linear correlation at different Arrhenius numbers, $\beta = 2$ deg/min

Ar	s	0.0	r^2
35	$5.59 \cdot 10^{-2}$	$-4.07 \cdot 10^{-2}$	0.9947
37	$4.14 \cdot 10^{-2}$	$-2.97 \cdot 10^{-2}$	0.9972
39	$3.10 \cdot 10^{-2}$	$-1.93 \cdot 10^{-2}$	0.9987
41	$2.26 \cdot 10^{-2}$	$-9.7 \cdot 10^{-3}$	0.9992
43	$1.66 \cdot 10^{-2}$	$-6.0 \cdot 10^{-4}$	0.9989
45	$1.22 \cdot 10^{-2}$	$8 \cdot 10^{-3}$	0.9979

From this fitting, the best Arrhenius number corresponds to Ar = 41, with $E_a/R = 12.218\ \mathrm{K}^{-1}$; the different values of s can be plotted *vs.* $1/\beta$, as shown in Fig. 3.

The linear regression fitting leads to the preexponential factor from the slope

$$s = \frac{A T_0 \exp(-\mathrm{Ar})}{C_0^{1-n}} = A\, T_0 \exp(-\mathrm{Ar})$$

where $A = 9{,}53 \cdot 10^{13}\ \mathrm{min}^{-1}$.

The experimental results for $\ln 1/(1-x)$ at different heating rates are shown in Fig. 4 versus

$$I = \frac{\int_1^y \exp(-\mathrm{Ar}/y)\,\mathrm{d}y}{\exp(-\mathrm{Ar})}.$$

A comparison with the experimental results given by Walker and Chadwick [13] for the depolymerization of trioxane between 40° and 95°, $E_a/R = 12.677\ \mathrm{K}^{-1}$ and $A = 10.03 \cdot 10^{13}\ \mathrm{min}^{-1}$, shows the feasibility of using programmed-temperature data to investigate kinetic reactions in the liquid phase.

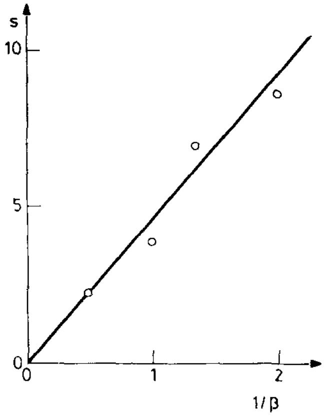

Fig. 3 "s" $vs.$ $1/\beta$ for the different experiments

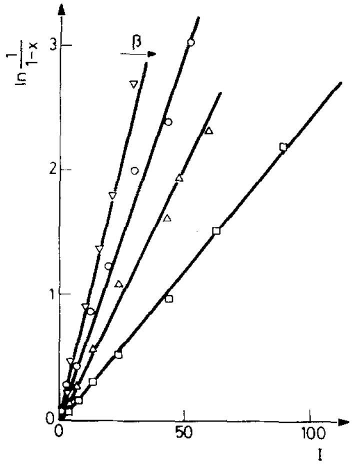

Fig. 4 Comparison between $\ln 1/(1-x)$ and I

It is very important that only one kinetic experiment permits determination of the kinetic model and kinetic parameters, leading to results which need a considerable experimental effort in the isothermal kinetic determination.

Thus, the programmed-temperature method to evaluate the kinetic model for a reaction in the liquid phase seems to be the optimum method to develop kinetic models in liquid-phase reactions.

The main problem in this method is the difficult analysis of complex kinetic models. A sequential model discrimination, which can be used for the determination of complex kinetic models, will be explained in subsequent papers.

References

1 A. A. Frost and R. G. Pearson, Kinetics and Mechanism, 2nd Edn., Wiley Interscience, New York 1961.
2 M. Boudart, Kinetics of Chemical processes, Prentice Hall, Englewood Cliffs, N.Y. 1968.
3 J. C. Jungers and L. Sajus, L'Analyse Cinètique de la Transformation Chimique, Techniq., Paris 1967.
4 E. Koch, Non-Isothermal Reaction Analysis, Academic press, N.Y. 1977.
5 E. Koch, Modelling of Chemical Reaction Systems, Springer Series in Chemical Physics, Vol. 18. Springer Verlag, N.Y. 1981.
6 S. W. Benson, Thermochemical Kinetics, Wiley Interscience, N.Y. 1968.
7 R. B. Root and R. A. Schmitz, AIChE J., 15 (1969) 670.
8 P. Hugo and W. Schaper, Ger. Chem. Eng., 3 (1980) 103.
9 H. Matsuda and S. Goto, Can. J. Chem. Eng., 62 (1984) 103.
10 H. Matsuda and S. Goto, Can. J. Chem. Eng., 62 (1984) 107.
11 M. I. Ortiz, A. Romero and A. Irabien, Thermochim. Acta, 94 (1985) 323.
12 Idem. Ibid., 94 (1985) 333.
13 J. F. Walker and A. F. Chadwick, Ind. Eng. Chem., 39 (1947) 974.
14 J. F. Walker "Formaldehyde" ACS Monograph 98, 489, Reinhold Pub., N.Y. 1944.

Zusammenfassung — Eine experimentelle Methode zur Bestimmung der kinetischen Daten von Reaktionen in flüssiger Phase bei linearer Temperaturerhöhung wird am Beispiel der Depolymerisation von Trioxan erklärt. Eine integrale kinetische Analyse der Daten wird ausgeführt, um das kinetische Modell und die kinetischen Parameter zu ermitteln. Bei unterschiedlicher Aufheizgeschwindigkeit zwischen 0,5 und 2 K/min ausgeführte Experimente ergaben ähnliche kinetische Parameter. Die erhaltenen Ergebnisse stimmen mit dem kinetischen Modell und den kinetischen Parametern, die durch isotherme kinetische Analyse erhalten wurden, überein. Die Temperaturprogrammierung scheint eine brauchbare, experimentelle Arbeit einsparende Methode zur schnellen Bestimmung des kinetischen Modells zu sein.

Резюме — Для объяснения реакции деполимеризации триоксана был использован экспериментальный метод определения кинетических данных реакций в жидкой фазе в условиях линейного нагрева. Для определения кинетической модели и кинетических параметров был проведен интегральный кинетический анализ данных. Эксперименты, проведенные при различных скоростях нагрева (0,5–2° в мин.), привели к одинаковым кинетическим параметрам. Полученные результаты хорошо согласуются с кинетической моделью и параметрами, полученными при изотермическом кинетическом анализе. Таким образом, метод программированного нагрева является полезным для быстрого определения кинетических моделей и не требует при этом проведения эксперимента.