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INTEGRAL KINETIC ANALYSIS FROM TEMPERATURE PROGRAMMED REACTION DATA: ALKALINE HYDROLYSIS OF ETHYL ACETATE AS TEST REACTION

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ABSTRACT

Kinetic modelling of the alkaline hydrolysis of ethyl acetate was performed using temperature programmed reaction (TPR) data.

The integral kinetic method for the analysis of TPR data, which was applied to the alkaline hydrolysis of ethyl acetate, allows a rapid and simple determination to be made of the reactivity, power kinetic model and kinetic parameters (pre-exponential factor and activation energy) in homogeneous liquid phase reactions, leading to useful information for the design, control or optimization of industrial chemical reactions.

The well-known kinetic behaviour of the alkaline hydrolysis of ethyl acetate was used as a reference system for the evaluation of TPR kinetic analysis.

INTRODUCTION

Most kinetic analyses of chemical reactions taking place in a homogeneous liquid phase have been carried out under isothermal conditions [1,2]. However, in recent years some effort has been directed to the application of non-isothermal methods for evaluating reaction rate models and kinetic parameters [3].

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Non-isothermal methods can be classified according to heat balance considerations as adiabatic methods (AM) and non-isothermal non-adiabatic methods (NINAM) where heat transfer takes place between the experimental system and its surroundings.

Adiabatic experiments using batch systems lead to temperature–time data from which the kinetic model and parameters for simple and complex systems can be extracted after application of a heat balance to relate temperature with conversion [4].

Similar procedures can be used in continuous systems [5]. The application of adiabatic methods to the determination of a kinetic model and parameters for reactor design may be justified on the following grounds: (i) industrial reactions are usually carried out under conditions which cannot be well described mathematically; (ii) the solutions may be highly concentrated or the solvent may even be absent; (iii) the raw materials may not be of technical quality; (iv) the reactor temperature may not be isothermal. In such cases, reactor design can only be achieved by applying a kinetic model with rather drastic simplifications. However, in AM the change in concentration with time is not usually determined, so that substantial errors may be obtained if the limitations of the method are not carefully considered.

An application of NINAM to the modelling of chemical reactions for practical purposes has been developed [6,7] for simple and complex liquid phase reactions, based on differential thermal analysis (DTA), in which neither the sample nor the reference material are heated and the temperature remains as isothermal as possible. Conversion–time curves are obtained through the difference between sample and reference temperatures, and by considering a quasi-isothermal behaviour, kinetic modelling of simple and complex reactions can be performed.

Similar procedures have been used by many workers to study the reaction kinetics of liquid phase reactions [8–11] under non-isothermal conditions, in the case of exothermic reactions. The main uncertainty of methods based on differential thermal analysis is related to the use of temperature instead of concentration in the evaluation of reaction rates.

NINAM has also been applied to gas–solid decomposition reactions using reaction data obtained by thermogravimetric procedures in which temperature programmed reactions (TPR) are carried out and the changing mass of solid is determined by weight [12]. However, only a few attempts to apply this method to liquid phase reactions have been reported.

Previous applications of TPR data to the determination of reaction rate expressions and the evaluation of kinetic parameters have been reported for the alkaline hydrolysis of ethyl acetate [13] and the acidic depolymerization of trioxane [14,15]. Although kinetic analysis using TPR experiments is far faster and experimentally simpler than the classical approach, Brown and Robinson [13] have found considerable deviations between the values obtained for the kinetic parameters and those reported for isothermal experiments [16] on the alkaline hydrolysis of ethyl acetate.

A simple method and a sequential method have been developed [17,18] and applied to a first-order reaction [14,15], in which a first approximation of the kinetic power model and parameters can be determined from a single experiment, followed by a better estimation of parameters, as well as supplementary evidence for the kinetic model, from a sequential design of experiments.

In this paper, a general method, which starts from a single TPR experiment and uses the initial concentration and/or heating rate as the dependent variable, is proposed for the development of kinetic models and the evaluation of kinetic parameters of industrial chemical reactions taking place in a homogeneous liquid phase.

The application of the method depends only on the previous knowledge of the reaction. It allows a rapid screening of the reactivity as a function of the temperature over the full range of concentrations of the industrial chemical reaction and provides an indication of the power expression to be used in the kinetic model and an approximation of the kinetic parameters from a single experiment. A sequential design of TPR experiments using the initial concentration as the variable can confirm previous hypotheses and increase the accuracy of the evaluated parameters. This is demonstrated in this work for the alkaline hydrolysis of ethyl acetate, previously analysed by Brown and Robinson [13].

EXPERIMENTAL METHODS

The experimental apparatus which allows a programmed temperature evolution of the homogeneous liquid phase reactions is similar to that reported earlier by Ortiz and Irabien [14].

A 250 cm^3 flask fitted with a magnetic stirrer, a reflux condenser, two thermoelements and an outlet for samples was positioned in a stirred water bath provided with external heating.

The two thermoelements were placed at different locations in the flask and both were in contact with the reaction mixture. One was also connected to the heating system which could be programmed for different rates of linear temperature increase (0.5, 0.75, 1.0 and 2.0 K min^{-1}). Preliminary experiments using water showed no difference in the local temperature of the stirred system at different positions if slopes were lower than 3 K min^{-1} or higher than 0.1 K min^{-1}.

Samples of 1 ml were taken from the flask with a syringe at known temperature–time values. The reaction was stopped by cooling and diluting the samples with a weighed amount of water. An acid–base titration of the diluted samples was used to determine the conversion of the ethyl acetate.

Analytical grade reagents, i.e. ethyl acetate, sodium hydroxide and hydrochloric acid, were used in the experiment.

RESULTS AND INTERPRETATION

Experiments at initial concentrations of ethyl acetate in the range 0.01–0.075 kmol m^{-3} were performed. In order to simplify the kinetic analysis, equimolar concentrations of ethyl acetate and sodium hydroxide were employed. TPR experiments were started at an initial temperature $T_0 = 298$ K and the heating rate was 0.5 K min^{-1}. Experimental results for the conversion of the reaction vs. dimensionless temperature are shown in Fig. 1.

Kinetic analysis for a single TPR experiment

The kinetic equation for a chemical reaction under isothermal conditions can be expressed by

$$r = \frac{1}{\nu_i}\frac{dC_i}{dt} = F(K_i, C_i) \tag{1}$$

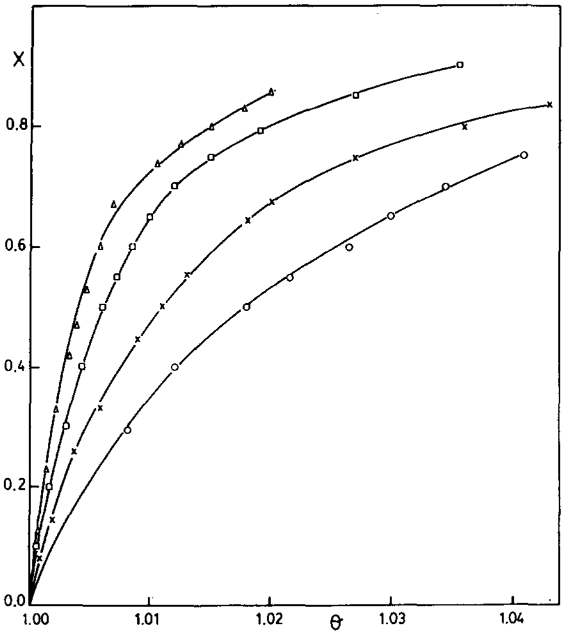

Fig. 1. Results of conversion vs. dimensionless temperature for experiments at different initial concentrations and $\beta = 0.5$ K min^{-1}; ○, 0.01 kmol m^{-3}; ×, 0.025 kmol m^{-3}; □, 0.05 kmol m^{-3}; △, 0.075 kmol m^{-3}.

where K_i represents the kinetic constants and C_i represents the concentrations involved in the kinetic expression.

For a kinetic model where variables are separable and where only one kinetic constant and concentration are involved in the rate equation

$$r = K(T) \cdot \mathrm{g}(C) \tag{2}$$

This equation is usually analysed using differential or integral methods to obtain the kinetic model $\mathrm{g}(C)$ and the true or apparent kinetic constant $K(T)$. Using isothermal experiments performed at different temperatures, the pre-exponential factor A and activation energy E are usually realized by fitting the kinetic constants obtained at different temperatures to the Arrhenius equation.

For experiments taking place under non-isothermal temperature conditions the integral method of kinetic data analysis can be applied, i.e.

$$-\frac{\mathrm{d}C}{\mathrm{g}(C)} = A \exp(-E/RT)\,\mathrm{d}t \tag{3}$$

which, on integrating, yields the relationship

$$C = \mathrm{NIF}(T, t) \tag{4}$$

where NIF is the non-isothermal function.

In experiments where a linear temperature programme has been carried out (TPR), the relationship between temperature and time can be expressed by $T = T_0 + \beta t$.

If this linear relationship is introduced into eqn. (3), the following expression is obtained

$$\int_{C_0}^{C} \frac{-\mathrm{d}C}{\mathrm{g}(C)} = \int_{T_0}^{T} \frac{A \exp(-E/RT)}{\beta}\,\mathrm{d}T \tag{5}$$

In chemical reaction engineering two types of approximate mathematical models are often applied to describe reacting systems of industrial interest: power equations and hyperbolic equations. It is well recognized that many industrial reactions, where highly concentrated solutions and raw materials of technical quality are used, cannot be easily described using mechanistic models; the application of power law equations for the reaction rate is a common approach, leading to apparent kinetic constants of great utility for design and optimization purposes.

Thus if $\mathrm{g}(C) = C^n$ is introduced into eqn. (5), then

$$\mathrm{f}(x) = \frac{AT_0}{\beta C_0^{1-n}} \int_1^{\theta} \exp(-\mathrm{Ar}_0/\theta)\,\mathrm{d}\theta \tag{6}$$

where $\mathrm{f}(x)$ is an integral function of the conversion, which depends on the experimental reaction order, i.e.

$$\mathrm{f}(x) = \begin{cases} \ln(1/1-x) & \text{for } n = 1 \\ \dfrac{1}{1-n}\left[1-(1-x)^{1-n}\right] & \text{for } n \neq 1 \end{cases} \tag{7}$$

Therefore according to eqn. (6) the general equation required to evaluate TPR data using a power law relation for the reaction rate can be expressed by

$$f(x) = \alpha \cdot I(\mathrm{Ar}_0, \theta) \tag{8}$$

The main advantage of using isothermal results to obtain kinetic information is that, because Ar_0/θ is constant, eqn. (6) can be integrated analytically. However, much more information is available from a single TPR experiment. In this case various approximation formulae or numerical methods can be used to evaluate the integral function I.

The integral function in eqn. (8) has been approximated by Coats and Redfern [19] as

$$I \simeq \frac{\exp(-\mathrm{Ar}_0)}{(\mathrm{Ar}_0 + 2)} \left\{ \theta^2 \frac{(\mathrm{Ar}_0 + 2)}{(\mathrm{Ar}_0 + 2\theta)} \exp[-\mathrm{Ar}_0(1-\theta)/\theta] - 1 \right\} \tag{9}$$

More recently Lee and Beck [20] obtained

$$I \simeq \frac{(\mathrm{Ar}_0 - 2)}{\mathrm{Ar}_0^2} \exp(-\mathrm{Ar}_0) \left\{ \frac{\theta^2(\mathrm{Ar}_0 - 2\theta)}{(\mathrm{Ar}_0 - 2)} \exp[-\mathrm{Ar}_0(1-\theta)/\theta] - 1 \right\} \tag{10}$$

and new approximation formulae for I are currently under consideration. If $\theta \ll \mathrm{Ar}_0$, both eqn. (9) and (10) reduce to

$$I \simeq \frac{\exp(-\mathrm{Ar}_0)}{\mathrm{Ar}_0} \left\{ \theta^2 \exp[-\mathrm{Ar}_0(1-\theta)/\theta] - 1 \right\} \tag{11}$$

The integral can also be evaluated by numerical methods (e.g. Simpson's rule).

Once the integral has been estimated, the slope α of the linear relationship between the conversion function $f(x)$ and I can be obtained by means of a simple linear regression computer program taking Ar_0 and n as parameters. Using the conversion–temperature data from Fig. 1, the program determines the correlation coefficient r^2 as well as the slope α for each combination of the parameters Ar_0 and n in the range $5 \leqslant \mathrm{Ar}_0 \leqslant 40$ and $0 \leqslant n \leqslant 2$ using four different methods for the evaluation of the integral term: Simpson's rule, the Lee–Beck approximation (eqn. (10)), the Coats and Redfern approximation (eqn. (9)) and the simplified $\theta \ll \mathrm{Ar}_0$ approximation (eqn. (11)).

The correlation coefficients obtained by fitting the results of the experiment with $C_0 = 0.01$ kmol m^{-3} are given in Table 1. The tabulated values indicate that a second-order model leads to the best fit independent of the evaluation method employed for the integral function. In addition, for all three reaction orders attempted the best Arrhenius number for each experiment is the one which gives the highest value of the correlation coefficient. The best-fit values of Ar_0 and α for different initial concentrations are

TABLE 1

Correlation coefficients of the linear regression fitting of eqn. (8) for $C_0 = 0.01$ kmol m^{-3} and $n = 0$, 1 and 2, using different methods for the evaluation of the integral

Ar_0	Correlation coefficient r^2			
	Simpson's rule	Lee–Beck (eqn. (10))	Coats–Redfern (eqn. (9))	Simplified (eqn. (11))
$n = 0$				
10	0.896	0.876	0.877	0.872
15	0.874	0.852	0.853	0.851
20	0.849	0.826	0.826	0.825
25	0.823	0.784	0.798	0.798
$n = 1$				
10	0.980	0.974	0.975	0.973
15	0.969	0.962	0.962	0.960
20	0.955	0.947	0.947	0.946
25	0.939	0.929	0.929	0.929
$n = 2$				
10	0.993	0.995	0.995	0.995
15	0.997	0.998	0.998	0.998
20	0.998	0.999	0.998	0.998
25	0.996	0.995	0.995	0.995

shown in Table 2. The activation energies and pre-exponential factors calculated by taking into account that $\alpha = AT_0/\beta C_0^{1-n}$ and $Ar_0 = E/RT_0$, are given in Table 3.

In order to obtain a common value for the pre-exponential factor, a linear fitting of α vs. C_0 is performed, and a slope corresponding to $A = 4.47 \times 10^7$ m^3 $kmol^{-1}$ s^{-1} is obtained. The linearity of this plot confirms that the best power law kinetic model corresponds to $n = 2$. However, there are important differences in the kinetic parameters obtained for the single runs where $38.4 \leqslant E \leqslant 48.0$ kJ mol^{-1} and $8.42 \times 10^5 \leqslant A \leqslant 6.10 \times 10^7$ m^3 $kmol^{-1}$ s^{-1}. These differences may be attributed to the experimental error (±5%) and the high sensitivity, particularly of the pre-exponential factor, to the fitted

TABLE 2

Slope and correlation coefficient of the linear regression fitting of eqn. (8) for each initial concentration

C_0 (kmol m^{-3})	Ar_0	α	r^2
0.01	20	2.18×10^{10}	0.9984
0.025	16	7.53×10^8	0.9978
0.050	20	7.83×10^{10}	0.9976
0.075	20	1.17×10^{11}	0.9939

TABLE 3

Calculated activation energies and pre-exponential factors for each initial concentration

C_0 (kmol m^{-3})	E (kJ mol^{-1})	A (m^3 kmol^{-1} s^{-1})
0.01	48.0	6.10×10^7
0.025	38.4	8.42×10^5
0.050	48.0	4.38×10^7
0.075	48.0	4.38×10^7

parameters. These errors can be decreased by replicating experiments or by using mean values of the activation energy ($\bar{E} = 45.60$ kJ mol^{-1}) and pre-exponential factor ($\bar{A} = 3.74 \times 10^7$ m^3 kmol^{-1} s^{-1}) for all experiments.

If different TPR curves at different initial concentrations are considered, then an integral kinetic analysis which takes conversions at the same temperatures for different initial concentrations can be performed to reduce the influence of the experimental error in the kinetic parameters. This leads to a single activation energy and pre-exponential factor for all the experiments.

Integral kinetic analysis at constant temperature from the curves for different initial concentrations

From the observation of the experimental curves obtained at different values of the initial concentration, it is possible to discriminate the possibility of order $n = 1$ from the others. If the curves x vs. θ are superimposed it may be concluded that the best kinetic model is of first order because in this case α does not depend on C_0.

Kinetic curves for the hydrolysis of ethyl acetate are not superimposed and therefore the $n = 1$ possibility can be discarded. From Fig. 1, a series of conversion values, one for each experiment, can be extracted for selected values of θ. These conversion values are shown in Table 4. For the kinetic analysis of these results, eqn. (6) can be expressed as

$$C_0^{1-n} = \frac{AT_0}{\beta\, \mathrm{f}(x)} \int_1^{\theta} \exp(-\mathrm{Ar}_0/\theta)\, \mathrm{d}\theta$$

$$= \gamma(\theta, A, T_0, \beta) \frac{1}{\mathrm{f}(x)} \tag{12}$$

The correlation coefficients obtained on carrying out a linear fit between C_0^{1-n} and $1/\mathrm{f}(x)$ for each dimensionless temperature and reaction order are shown in Table 5, indicating that the best value of n corresponds to a second-order model.

Since $\gamma = AT_0\mathrm{I}(\mathrm{Ar}_0, \theta)/\beta$, the integral I can be evaluated for each θ chosen above by trying selected values of the Arrhenius number Ar_0. The

TABLE 4

Conversion values at constant dimensionless temperature taken from Fig. 1

C_0 (kmol m^{-3})	θ	x
0.01	1.0075	0.28
0.025	1.0075	0.385
0.05	1.0075	0.56
0.075	1.0075	0.667
0.01	1.01	0.35
0.025	1.01	0.475
0.05	1.01	0.65
0.075	1.01	0.725
0.01	1.0125	0.41
0.025	1.0125	0.54
0.05	1.0125	0.707
0.075	1.0125	0.767
0.01	1.015	0.455
0.025	1.015	0.59
0.05	1.015	0.75
0.075	1.015	0.797
0.01	1.019	0.526
0.025	1.019	0.66
0.05	1.019	0.79
0.075	1.019	0.845

fitted γ values can then be refitted by linear regression as a function of I to obtain the best-fit slope AT_0/β. The correlation coefficients obtained for four values of Ar_0 are listed in Table 6.

TABLE 5

Correlation coefficients of the linear regression fitting of C_0^{1-n} vs. $1/\mathrm{f}(x)$ at constant dimensionless temperature

θ	n	r^2
1.0075	2	0.990
1.01	2	0.996
1.0125	2	0.994
1.015	2	0.989
1.019	2	0.998
1.0075	1	0.998
1.01	1	0.988
1.0125	1	0.980
1.015	1	0.969
1.019	1	0.985
1.0075	0	0.987
1.01	0	0.961
1.0125	0	0.945
1.015	0	0.927
1.019	0	0.933

TABLE 6

Linear fitting of eqn. (14) using the Arrhenius number as parameter for the evaluation of the integral function

Ar_0	AT_0/β	r^2
16	2.61×10^{10}	0.995
18	1.88×10^{11}	0.995
20	1.353×10^{12}	0.996
23	2.404×10^{13}	0.995

Finally, from the Arrhenius number which corresponds to the maximum correlation coefficient, the best activation energy for all the experiments is calculated as $E = 48.00$ kJ mol^{-1}. From the slope obtained for this value of Ar_0, the pre-exponential factor A is found to be $A = 4.05\times10^7$ m^3 kmol^{-1} s^{-1}.

DISCUSSION AND CONCLUSIONS

Table 7 shows a comparison of the values given in the literature for the kinetic parameters of ethyl acetate hydrolysis from isothermal [16] and non-isothermal [13] experiments with the results obtained in this work using kinetic analysis of simple TPR experiments and a pseudo-isothermal analysis from TPR curves obtained at different initial concentrations.

From the analysis of a single TPR experiment, the power kinetic model and parameters can be evaluated for a second-order reaction as shown in this paper and for a first-order reaction [14]. However, a very strong influence of the experimental error has been detected in experiments starting

TABLE 7

Comparison of different kinetic studies

Reference	E (kJ mol^{-1})	A (m^3 kmol^{-1} s^{-1})
David and Villermaux, 1980		
Isothermal	48.75	4.36×10^7
Brown and Robinson, 1986		
Isothermal	40.69	3.05×10^6
TPR analysis	69.64	1.44×10^{14}
TPR analysis	52.43	1.12×10^8
This work		
Kinetic analysis of single runs at different concentrations	$38.4 \leqslant E \leqslant 48.0$	$8.42\times10^5 \leqslant A \leqslant 6.10\times10^7$
Mean values	45.6	4.83×10^7
Kinetic analysis at constant temperature of the curves at different concentration	48.0	4.05×10^7

at different values of reagent concentration; this has an important influence on the activation energy and pre-exponential factor due to the sensitivity of the non-isothermal kinetic analysis of a single experiment. This fact explains the large differences observed between the values of the kinetic parameters of the alkaline hydrolysis of ethyl acetate obtained previously by non-linear regression fitting of TPR data [13] and those obtained under isothermal conditions [16].

The sensitivity to the experimental error can be decreased substantially using a sequential discrimination method. This is applied to a set of TPR experiments which are performed using the initial concentration and/or heating rate as experimental variable. A pseudo-isothermal analysis of the curves obtained at different initial concentrations is conducted.

Therefore, this work leads to two main conclusions.

(i) TPR methods retain the advantages of non-isothermal methods related to the application to industrial reactions, i.e. the feasibility of working under conditions similar to those prevailing during the industrial process, the rapid evaluation of the reactivity and simple kinetic models and the enhancement of the accuracy of the determination of the kinetic model since both temperature and concentration are measured with time.

(ii) An integral kinetic analysis of TPR data performed using simple computer techniques, permits the evaluation of kinetic parameters more quickly than with conventional isothermal techniques, as demonstrated for the alkaline hydrolysis of ethyl acetate used as a test reaction. The reported sequential discrimination method for the interpretation of TPR data decreases the influence of the experimental error and provides supplementary evidence for the kinetic model which enhances the accuracy of the parameters. A third step of classical isothermal experiments may be necessary if results are not conclusive for design, control or optimization purposes.

Non-linear methods of parameter optimization can be used to obtain the best value of the parameters, once the kinetic model and starting parameters for the optimization have been obtained following the simple procedure shown in this work.

NOMENCLATURE

A	pre-exponential factor ((kmol $m^{-3})^{1-n}$ s^{-1})
Ar	Arrhenius number, E/RT
C	concentration (kmol m^{-3})
E	activation energy (kJ mol^{-1})
I	integral function ($\int_1^\theta \exp - (\mathrm{Ar}_0/\theta)\, d\theta$)
K	kinetic constant ((kmol $m^{-3})^{1-n}$ s^{-1})
n	reaction order
r	reaction rate (kmol m^{-3} s^{-1})

r^2	correlation coefficient
t	time (s)
T	temperature (K)
x	dimensionless conversion

Greek letters

α	slope in eqn. (8) ($AT_0/\beta C_0^{1-n}$)
β	heating rate (K min^{-1})
γ	slope in eqn. (12) ($AT_0\mathrm{I}(\mathrm{Ar}_0, \theta)/\beta$)
θ	dimensionless temperature, T/T_0
ν	stoichiometric coefficient

Subscripts

0	refers to initial conditions
i	refers to a reagent or a product

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