

## KINETIC APPLICATIONS OF THERMAL ANALYSIS

### A Comparison of Dynamic and Isothermal Methods\*

*P. M. D. Benoit, R. G. Ferrillo and A. H. Granzow*

AMERICAN CYANAMID COMPANY CHEMICAL RESEARCH DIVISION  
1937 WEST MAIN STREET P.O. BOX 60 STAMFORD, CT 06904-0060 U.S.A.

(Received September 28, 1984; in revised form January 29, 1985)

A study was undertaken to compare two computational methods of estimating kinetic parameters from thermoanalytical experiments. Examples illustrating the relationship between reaction complexity and validity of isothermal vs. non-isothermal kinetic analyses will be presented. Thermal decomposition of several compounds was studied both by isothermal and dynamic thermogravimetry (TG). For the isothermal runs, reaction order and activation energy were estimated using established methods. For the dynamic runs, the statistical method of nonlinear least squares was used to estimate all three kinetic parameters of the  $n$ th order decomposition reaction and their individual 95% confidence intervals. Both methods assumed Arrhenius temperature dependence.

There has been considerable discussion in the literature concerning the validity of kinetic data obtained by thermal analysis under non-isothermal conditions [1]. The main objections against this approach are the following:

Non-isothermal experiments imply the simultaneous change of three variables—degree of conversion, time, and temperature. This increases the error in determining reaction order and Arrhenius parameters. The error in the determination of reaction order is especially critical for condensed phase decompositions because they often exhibit fractional reaction orders. Similarly, kinetic analysis of non-isothermal data is not possible if the reaction kinetics change within the temperature range under consideration. For decomposition reactions, one often observes transitions from zero to first order at higher temperature or at higher degree of conversion. This behavior can be due to a change in the rate-limiting step in the decomposition. The non-isothermal method is also not applicable in the case of reverse parallel reactions. Apparently, occurrence of induction periods as observed in many condensed phase decompositions cannot be detected reliably [2].

\* Presented at the 13th North American Thermal Analysis Society Conference, Philadelphia, PA 23–26 September 1984.

Aside from these intrinsic limitations, experimental restrictions on the validity of the non-isothermal kinetics have to be considered. During non-isothermal experiments, a lag exists between the nominal temperature of the furnace and the actual sample temperature. This lag results in a temperature gradient within the sample which might seriously distort any kinetic data extracted from non-isothermal experiments.

We will show that the non-isothermal method of kinetic analysis should be preceded by specific isothermal studies to resolve the problems just discussed. Specifically, isothermal runs must be done at the upper and lower limits of the intended non-isothermal temperature range to verify that the kinetic order remains constant throughout. Additionally, these isothermal studies should reveal any reversible, parallel or autocatalytical processes that are not accounted for in the simple  $n$ th order decomposition reaction model for the non-isothermal data. After these issues have been addressed, then the non-isothermal experiments can be employed to estimate reliably the frequency factor and the activation energy. In the case of large numbers of similar samples, this approach would then result in a considerable time saving, as compared to the isothermal approach.

## **Experimental**

### *Materials*

All materials were research samples by American Cyanamid company.

### *Procedures*

Thermogravimetric instrumentation, models TGS-1 and TGS-2 by Perkin-Elmer Corporation, was used in this study. The temperature scale of the instruments was calibrated using Curie point standards according to the manufacturer's specification. Further details have been described elsewhere [2, 3].

### *Isothermal method*

Experimental details have been described elsewhere [2, 3].

### *Non-isothermal method*

A FORTRAN program performs the nonlinear least squares procedure using the modified Gauss-Newton method and the Watts and Bates convergence criterion [4-8]. All computing was done on a DEC System-10 computer.

## Results and discussion

### *Mathematical analysis*

The difficulty of mathematical analysis of non-isothermally derived data has generally been a deterrent to the use of non-isothermal methods for estimating kinetic parameters [9]. Approximate estimation methods exist but have been only moderately successful due to their inherent assumptions [9, 10]. Techniques for isothermal data involve only one variable, time, and, therefore, are considerably simpler.

The non-linear least squares method is a statistical procedure that evaluates all parameters simultaneously for the best fit to the data. This method was applied to the non-isothermal data to estimate the three kinetic parameters. Since the kinetics model is a differential equation that cannot be solved analytically in the non-isothermal case, some numerical complexities arise, e.g. numerical integration of the differential equation and numerical differentiation of the model with respect to each parameter. Another difficulty is the extremely high statistical correlation between the parameters, especially frequency factor and activation energy. A transformation for frequency factor was used to reduce the correlations and, therefore, to speed the convergence to reliable parameter values. These numerical complexities had to be addressed in order to solve this problem successfully.

### *Mathematical derivation*

The curve heights from the TG experiments are proportional to the weight percent lost,  $x$ , the time in seconds,  $t$ , and the temperature in degrees K,  $T$ .

The model for the reaction is the  $n$ th order decomposition reaction assuming Arrhenius temperature dependence. That is

$$dx/dt = Z(1-x)^n \exp[-E/(RT)] \quad (1)$$

where  $x=0$  at  $t=0$ ,  $T=T_0$ ,  $Z$ =frequency factor,  $n$ =reaction order,  $R$ =gas constant, and  $e$ =activation energy. To decrease the correlation between the estimated parameters, and thereby improve the conditioning of the problem, the following transformation was used:

$$\ln \zeta = \ln Z - E/[R(\overline{1/T})] \quad (2)$$

where  $(\overline{1/T})$  is the average of the inverse temperatures. Substituting the transformation (2) into Eq. (1) gives the following form of the model:

$$dx/dt = (1-x)^n \exp\{\ln \zeta - E/R[1/T - (\overline{1/T})]\} \quad (3)$$

where  $x = 0$  at  $t = 0$  and  $T = T_0$ : the model is fitted by nonlinear least squares to find the set of parameters  $n$ ,  $E$ , and  $\ln \zeta$  that best fit the data.

Because Eq. (3) is a differential equation that cannot be solved analytically, numerical solution is required to calculate the predicted  $x$  at each temperature point. The Runge-Kutta method was used. Nonlinear least squares requires partial derivatives of the model with respect to each parameter evaluated at each temperature point. As before, these partials cannot be found analytically, but must be approximated by numerical differentiation. Lastly, initial estimates for the parameters are required to start the iteration procedure. An initial estimation scheme using the natural logarithm of Eq. (3) gives a function that is linear in the three parameters  $n$ ,  $\ln \zeta$ ,  $E$ . This linear model is then fitted by multiple linear least squares to produce the initial estimates. Although the initial model ignores the error structure of the data, it provides a starting point. Generally, it was found that the initial estimates from the logarithmic model were not as good as expected and were often surprisingly far from the final estimates. Once the nonlinear least squares procedure converges, estimates for  $n$ ,  $E$ ,  $\ln \zeta$ , and their individual 95% confidence intervals are estimated.

#### *Thermoanalytical applications*

A comparison of the isothermal and non-isothermal computational methods as applied to several phosphorus-containing compounds has been attempted. These compounds include phenylmethylene-2,2-dimethyltrimethylene phosphonate, I, [(1,4-phenylene)-dimethylene] bis [2,2-dimethyltrimethylene phosphonate], II, and [(2,5-dimethyl-1,4-phenylene) dimethylene] bis [2,2-dimethyltrimethylene phos-

**Table 1** Isothermal vs. non-isothermal data

Compound	Activation energy, kJ/mole		Reaction order	
	Isothermal	Non-isothermal	Isothermal	Non-isothermal
I	70	70	0	0
II	162	—	PT	negative
III	198	—	0	negative
IV	(150)	240	PT	1.2

phonate], III, and ethylene bis[tris(2-cyanoethyl)] phosphonium bromide, IV. The structures of the four compounds are depicted in Fig. 1. Kinetic data for these compounds obtained by isothermal methods have been previously reported [3, 4].

A comparison of kinetic data obtained by isothermal and non-isothermal methods is summarized in Table 1.

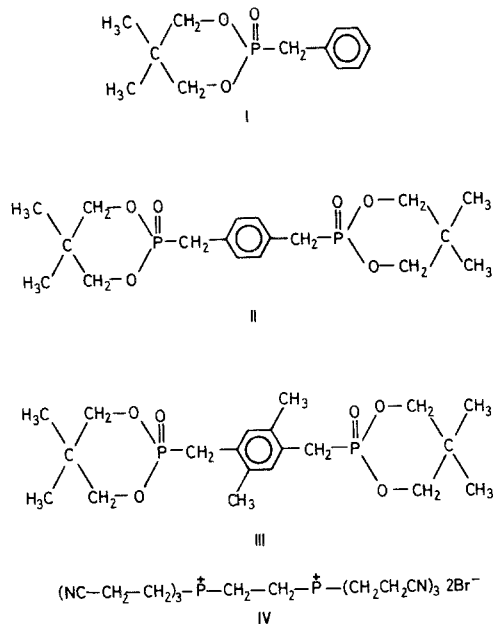


Fig. 1 Structures: compounds I, II, III, and IV

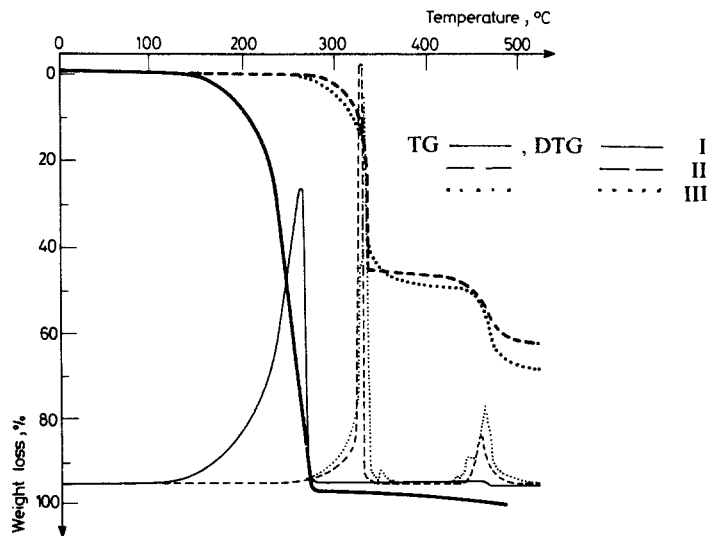


Fig. 2 Dynamic TG thermal curves of compounds I, II, and III in nitrogen. Heating rate: 10 deg/min

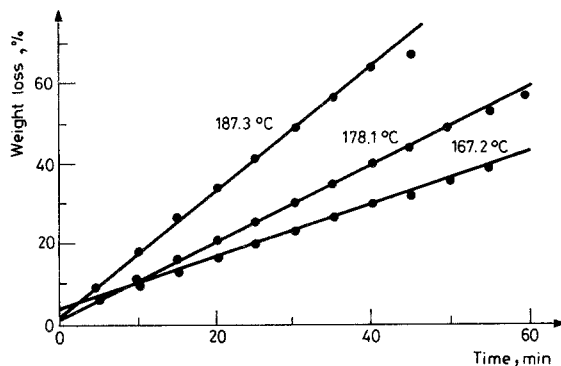


Fig. 3 Isothermal decomposition curves of I: nitrogen atmosphere

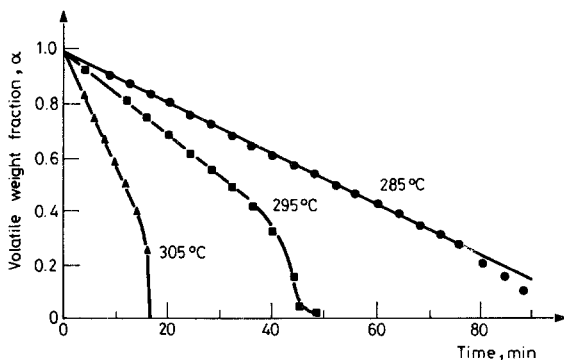


Fig. 4 Isothermal decomposition curves of III: nitrogen atmosphere

Dynamic TG/DTG thermal curves for compounds I, II, and III are shown in Fig. 2. For compound I, volatilization leaving no residue occurs. The shape of the DTG curve suggests an apparent reaction order of zero for the volatilization. Under isothermal conditions, as shown in Fig. 3, the decomposition of I is linear with time for the range 167–187°. From the apparent zero order rate constant, an activation energy of  $E = 70$  kJ/mole is calculated. When analyzed by the non-isothermal computational method, a zero reaction order and the activation energy of 70 kJ/mole are obtained. This shows that excellent agreement between isothermal and non-isothermal methods is obtained for simple zero order processes, such as evaporation, which involve no bond breaking in the condensed phase.

Dynamic TG/DTG curves for II and III are more complex. For both compounds, decomposition involves multi-step processes. The DTG curves indicate at least two processes to describe the decomposition reaction. The complexity of these curves suggests an isothermal approach to arrive at a kinetic model.

For III, the decomposition kinetics between 285–305°, as determined by isothermal methods, are zero order, Fig. 4, [4]. However, as the temperature is

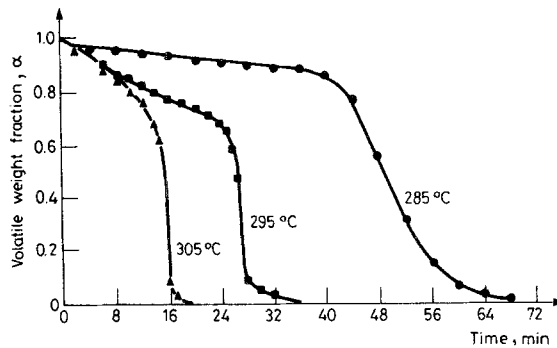


Fig. 5 Isothermal decomposition curves of II: nitrogen atmosphere

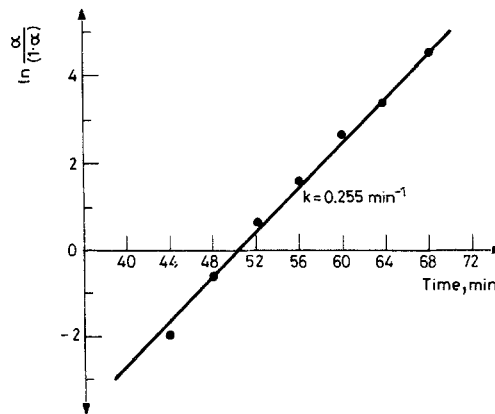


Fig. 6 Prout-Tompkins plot for the decomposition of II: 285°C, nitrogen atmosphere

increased, a change in the volatilization kinetics is observed. This suggests the existence of two consecutive reactions with different activation energies. This assumption is verified by the dynamic DTG thermal curve which is very steep and is multi-peaked. Our non-isothermal method only allows for the simple decomposition model and, therefore, any multiple processes will give unreasonable results. Negative reaction orders are obtained, indicating the inadequacy of the simple decomposition model.

Isothermal kinetic analysis of II in the temperature range 285–305° results in a weight loss vs. time curve that is sigmoid, Fig. 5. As shown in Fig. 6, a sigmoid curve shape can be reconciled by a solid state analysis according to a Prout-Tompkins mechanism [13]. For the same reasons as III, the non-isothermal approach could not fit a decomposition model to this type of process and gave spurious results.

When studied under isothermal conditions, IV also yields a sigmoid thermal curve, suggesting again an autocatalytic solid state reaction, Fig. 7, [4]. This

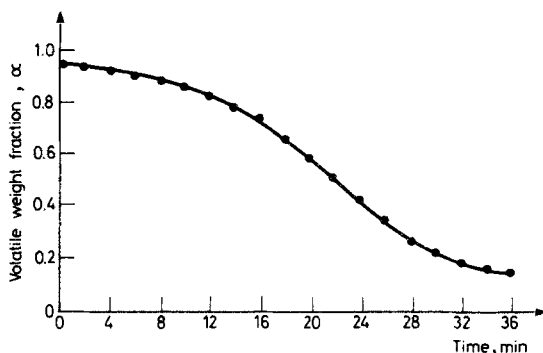


Fig. 7 Isothermal decomposition curve of IV: 285°C, argon atmosphere

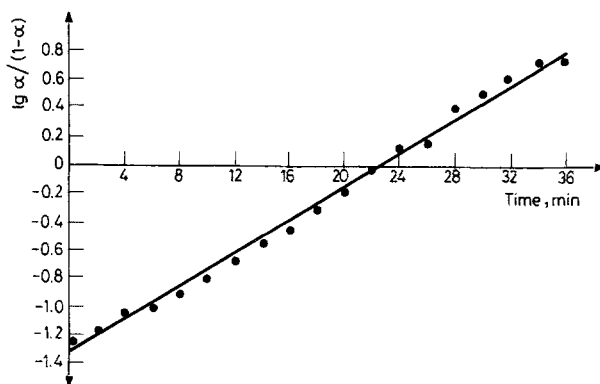


Fig. 8 Prout-Tompkins plot for the decomposition of IV: 285°C, argon atmosphere

reaction, as well as the decomposition of compound II, obeys a Prout-Tompkins model [13]. A plot of a  $\lg \alpha/(1-\alpha)$ , where  $\alpha$  = volatile weight fraction, vs. time is linear over approximately 90% of the reaction, as required by the Prout-Tompkins model, Fig. 8. In this case, the non-isothermal approach gives approximately a first order reaction ( $n=1.2$ ), but the excessively high activation energy, 240 kJ/mole, indicated that the model was not valid. As shown with data from compound II, solid state decomposition reactions are not readily accommodated by non-isothermal computational methods.

## Conclusions

1. Any non-isothermal method of kinetic analysis should be preceded by specific isothermal studies to verify that the kinetic order remains constant throughout the temperature range of interest.



2. Only isothermal studies reveal any reversible, parallel, or autocatalytic processes that are not accounted for in the simple  $n$ th order reaction decomposition model for non-isothermal data.

3. Excellent agreement between isothermal and non-isothermal methods is obtained for simple kinetic processes, such as zero order reactions.

4. Solid state decomposition reactions, which are often autocatalytic, are not readily accommodated by non-isothermal computational methods.

## References

- 1 C. H. Bamford and C. F. H. Tipper, "Comprehensive Chemical Kinetics", Vol. 22 Elsevier Scientific Publishing Co., Amsterdam-Oxford-New York 1980.
- 2 R. G. Ferrillo and A. H. Granzow, *Thermochim. Acta*, 38 (1980), 27-36.
- 3 R. G. Ferrillo and A. H. Granzow, *J. Thermal Anal.*, 29 (1984) 1237.
- 4 P. M. D. Benoit and D. W. Behnken, American Cyanamid Internal Report, 1982.
- 5 H. O. Hartley, *Technometrics*, 3 (1961) 269-280.
- 6 G. E. P. Box, *Annals of the New York Academy of Sciences*, 86 (1960) 792-816.
- 7 Y. Bard, "Nonlinear Parameter Estimation", Academic Press, New York 1974.
- 8 D. M. Bates and D. G. Watts, *Technometrics*, 23 (1981) 179-183.
- 9 E. A. Turi, Editor, "Thermal Characterization of Polymeric Materials", Academic Press, New York 1981.
- 10 R. N. Rogers and L. C. Smith, *Thermochim. Acta*, 1 (1970) 1.
- 11 E. G. Prout and F. C. Tompkins, *Trans. Faraday Soc.*, 40 (1944) 488.

**Zusammenfassung** — Es wurde eine Untersuchung zum Vergleich von zwei Methoden zur Berechnung von kinetischen Parametern aus Ergebnissen thermoanalytischer Experimente unternommen. Beispiele werden angegeben, die die Beziehung zwischen isothermer und nichtisothermer kinetischer Analyse in Bezug auf Komplexizität der Reaktion und Gültigkeit illustrieren. Die thermische Zersetzung verschiedener Verbindungen wurde mittels isothermer und dynamischer Thermogravimetrie (TG) untersucht. Aus den isothermen Versuchsergebnissen wurden die Reaktionsordnung und Aktivierungsenergie nach den üblichen Methoden bestimmt. Aus den dynamischen Versuchsdaten wurden alle drei kinetischen Parameter der Reaktion  $n$ -ter Ordnung und deren individuelle 95%-Konfidenzintervalle nach der Methode der kleinsten Fehlerquadrate ermittelt. Beide Methoden setzen eine Temperaturabhängigkeit entsprechend der Arrhenius-Gleichung voraus.

**Резюме** — Проведено сопоставление двух вычислительных методов, используемых для определения кинетических параметров на основе термоаналитических данных. Представлены примеры, показывающие взаимосвязь между сложностью реакции и обоснованностью изотермического кинетического анализа по отношению к неизотермическому. Термическое разложение нескольких соединений было изучено как изотермическим, так и динамическим методами ТГ. Для изотермического режима по известным методам были вычислены порядок реакции и энергия активации. Для динамического режима был использован статистический метод нелинейных наименьших квадратов для оценки всех трех кинетических параметров  $n$ -го порядка реакции разложения и их 95% доверительных интервалов. В обоих методах предполагалась аррениусовская температурная зависимость.