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Non-isothermal spectrophotometric kinetics applied to inorganic reactions

Giuseppe Alibrandi

Dipartimento di Chimica Inorganica, Analitica e Struttura Molecolare, Università di Messina, Salita Sperone 31, Vill. S. Agata, 98166 Messina (Italy)

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Abstract

Kinetic constants and activation parameters of some inorganic reactions in solution have been obtained very easily and with great accuracy from variable temperature spectrophotometric kinetic data using a method based on non-isothermal analysis. The reactions studied under various experimental conditions to test the method were the *cis–trans* isomerization of the cation $[Pt(PEt_3)_2(CH_3)(C_2H_5OH)]^+$ in ethanol and the thermal decomposition of the alkyl solvent species *trans*-$[Pt(PEt_3)_2(n\text{-}C_4H_9)(CH_3OH)]^+$ to yield the *trans*-hydride $[Pt(PEt_3)_2(H)(CH_3OH)]^+$ in methanol. The results are compared with those obtained by the traditional isothermal method. A suitable experimental apparatus and software is described for routine measurements.

Key words: Kinetics and mechanism; Isomerization; Platinum complexes; Alkyl complexes; Solvato complexes

Introduction

The theory of non-isothermal analysis was developed several years ago [1] and it is widely used in thermochemistry. There have been some suggestions that the method could be extended to the determination of the activation parameters of reactions in solution [2–4] but up to now almost all the data that appear in the literature seem to have been obtained by traditional isothermal kinetics.

The aim of this paper is to show that the non-isothermal method permits the collection of the kinetic data in a much shorter time and with a greater accuracy than with the usual isothermal technique, using an experimental apparatus that nowadays can be considered routine.

The main feature of the method is to change the way of producing the kinetic data. Instead of obtaining single values of rate constants at single different temperatures, the aim is to produce in a single short experiment a $k(T)$ profile (i.e. a whole set of rate constants in a definite temperature range). This $k(T)$ profile can be either used to calculate the activation parameters for unimolecular reactions or, for more complicated systems, it offers a complete and detailed picture of the temperature dependence of the rate constant.

The experimental apparatus necessary to collect the primary spectrophotometric data requires only a few modifications of a conventional spectrophotometer. The gradient of the temperature inside the spectrophotometric cell can be obtained with a temperature programmer such as those now available commercially for the measurement of the melting point of DNA [5]. The automatic transfer of the absorbance versus time data to a microcomputer and the fast processing by appropriate algorithms permit the recording and processing of the kinetic data in a time as short as twenty minutes.

Experimental

The synthesis and characterization of the compounds studied and their reaction mechanisms have been reported elsewhere [6, 7].

Kinetic runs were carried out using a Perkin-Elmer Lambda 3 spectrophotometer connected to a 486/DX-IBM microcomputer and equipped with a cell compartment thermostated by a Perkin-Elmer PTP (Peltier temperature programmer). The temperature control was checked by a thermocouple inserted into the spectrophotometric cell and connected to a recorder. The thermal and chemical homogeneity of the solution was ensured by magnetic stirring. The reactions were started

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at a suitable low temperature where the rate was sufficiently low in order to ensure a good initial thermostating and to avoid the difficulty of the dead time before reaching the linear part of the temperature programme. In this first part of the kinetics the cell compartment was maintained under dry air to avoid condensation of humidity on the cell walls. The automatic acquisition of the absorbance–time data was made using the Perkin-Elmer PECSS programme. Data processing was made on the microcomputer using the Jandel Scientific PeakFit programme or on a Macintosh LC III using the Synergy Software KaleidaGraph programme.

Results and discussion

The reactions studied were

$$\textit{cis}\text{-}[\mathrm{PtL_2(Me)(EtOH)}]^+ \longrightarrow \textit{trans}\text{-}[\mathrm{PtL_2(Me)(EtOH)}]^+ \qquad (1)$$

$$\textit{trans}\text{-}[\mathrm{PtL_2(n\text{-}Bu)(MeOH)}]^+ \longrightarrow \textit{trans}\text{-}[\mathrm{PtL_2(H)(MeOH)}]^+ + \text{butenes} \qquad (2)$$

($L = PEt_3$) whose mechanisms have been studied in great detail and appear to be well established.

Two spectrophotometric non-isothermal kinetics were performed for reaction (1), in ethanol. Taking advantage of the presence in the spectral changes of an isosbestic point at 248 nm, the first kinetic run was followed at 238 nm with a spectral change of about 0.5 absorbance units. The second run was followed at 263 nm with a variation of less than 0.2 absorbance units in the opposite direction. For both experiments the rate of increase of the temperature with time was 1.94 K/min. Reaction (2) was carried out in methanol and followed at 240 nm with temperature gradients of 2.0 K/min and 0.99 K/min.

Consider a first-order reaction (3)

$$\mathrm{A} \longrightarrow \mathrm{B} \qquad (3)$$

For this reaction the rate law is

$$v = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}] \qquad (4)$$

and the integrated form at constant temperature takes the familiar form

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp(-kt) \qquad (5)$$

which describes the exponential decrease of [A] with time. If the optical density is the physical parameter chosen to follow the kinetics, eqn. (5) can be modified to give

$$D_t = (D_0 - D_\infty)\exp(-kt) + D_\infty \qquad (6)$$

where D_t, D_0 and D_∞ are the optical densities at time t, at the beginning and at the end of the reaction, respectively.

It is possible to calculate the activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$, using the Eyring equation (eqn. (7)), from several values of k, taken at different temperatures.

$$k = \frac{\mathbf{k}T}{h}\exp\left[\frac{\Delta S^{\neq}}{R}\right]\exp\left[-\frac{\Delta H^{\neq}}{RT}\right] \qquad (7)$$

If the temperature is changed during the course of the reaction, eqn. (4) maintains its validity but, under these circumstances, the rate depends on contributions from two varying factors, $[\mathrm{A}] = [\mathrm{A}](t)$ and $k[T(t)]$. The first decreases with time while the second increases as the temperature increases. The simplest way of increasing the temperature of a reacting system is to impose a linear variation defined by the relation $T = T_0 + \alpha t$.

Introducing this expression into eqn. (7) and rearranging, eqn. (8) is obtained.

$$-\frac{d[\mathrm{A}]}{dt} = \frac{\mathbf{k}(T_0+\alpha t)}{h}\exp\left[\frac{\Delta S^{\neq}}{R}\right]\exp\left[-\frac{\Delta H^{\neq}}{R(T_0+\alpha t)}\right][\mathrm{A}] \qquad (8)$$

It is now possible, as for eqn. (5), to describe the variation of [A] with time using eqn. (9) which is an integrated form of eqn. (8).

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp\left\{-\frac{\mathbf{k}}{h}\exp\left[\frac{\Delta S^{\neq}}{R}\right]\int_0^t (T_0+\alpha t) \times \exp\left[-\frac{\Delta H^{\neq}}{R(T_0+\alpha t)}\right]dt\right\} \qquad (9)$$

Replacing the concentrations with the optical densities, eqn. (9) takes the form*

$$D_t = (D_0 - D_\infty)\exp\left\{-\frac{\mathbf{k}}{h}\exp\left[\frac{\Delta S^{\neq}}{R}\right]\int_0^t (T_0+\alpha t) \times \exp\left[-\frac{\Delta H^{\neq}}{R(T_0+\alpha t)}\right]dt\right\} + D_\infty \qquad (10)$$

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*Due to the relatively short range of temperature usually considered for the determination of the activation parameters, small effects on the optical density caused by the temperature dependence of the molar extinction coefficient and by the variation of the concentration of the absorbing species caused by the thermal expansion of the solvents are not considered in this text. For the same reason $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are also considered constant. Any deviation from this pattern of behaviour is evidentiated by a linearization of the $k(T)$ profile as obtained by the differential method.

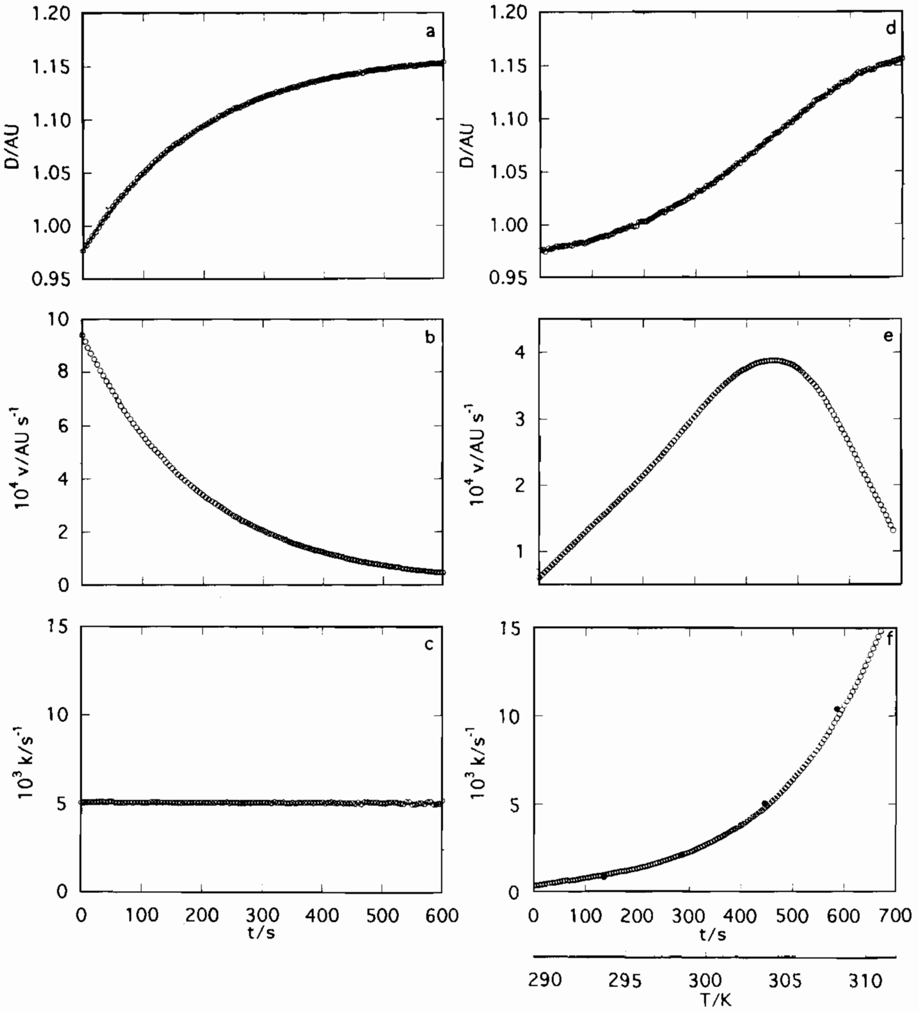

Fig. 1. Change in optical density at 263 nm during the *cis* to *trans* isomerization of *cis*-$[Pt(PEt_3)_2(CH_3)(C_2H_5OH)]^+$ in ethanol (a) under isothermal (289.3 K) and (d) non-isothermal (T (K) = 289.3 + 0.0323 t (s)) conditions and relative trend of rates of reaction and values of rate constants as obtained respectively by differentiation of the kinetic curves (b and e) and dividing then by $(D_t - D_\infty)$ (c and f). Solid lines are the theoretical curves obtained by the best fitting to eqns. (6) and (9) respectively. Solid circles are for isothermal kinetics.

The integrals which are involved in eqns. (9) and (10) cannot be solved in terms of elementary functions.

The experimental results of kinetic runs carried out under isothermal and non-isothermal conditions will be used to underline the main differences between the two methods. The results are illustrated in Fig. 1.

Figure 1(a) shows the exponential increase of the optical density for reaction (1) according to eqn. (6). The value of $k = 5.08 \times 10^{-3}$ s^{-1} was obtained from a non-linear least-squares fitting of the data to eqn. (6), with k, D_0 and D_∞ as the parameters to be optimized. The rate of variation of the optical density (dD_t/dt) was obtained from the derivative of the first curve (Fig. 1(b)) and is proportional to the rate of reaction. The rate constant k (Fig. 1(c)) can be obtained by dividing the rate of variation of D by the normalized value of the optical density $(D_t - D_\infty)$*.

$$k = \left| \frac{1}{D_t - D_\infty} \frac{dD_t}{dt} \right| \tag{11}$$

Figure 1(d) shows the D_t–t profile, obtained according to eqn. (10), which has the shape of a sigmoid with an inflection point. The first derivative of the curve, shown in Fig. 1(e), was obtained by the Savitzky–Golay method [8] and is particularly informative about the way in which the rate changes with time. Initially the rate increases because the decrease of [A] is overwhelmed by the acceleration due to the increase of

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*Equation (11) is obtained from the rate law in the form $-(1/[A])\ d[A]/dt = k$ replacing the concentration with the optical density.

TABLE 1. Activation parameters for the *cis–trans* isomerization of *cis*-$[\mathrm{Pt(PEt_3)_2(CH_3)(C_2H_5OH)}]^+$ in ethanol (reaction (1)) and the thermal decomposition of *trans*-$[\mathrm{Pt(PEt_3)_2(n\text{-}C_4H_9)(CH_3OH)}]^+$ in methanol (reaction (2)) obtained under isothermal and non-isothermal conditions and using different processing methods

	Reaction (1)		Reaction (2)	
	$\Delta H^{\neq}$ (kJ $\mathrm{mol^{-1}}$)	$\Delta S^{\neq}$ (J $\mathrm{K^{-1}\ mol^{-1}}$)	$\Delta H^{\neq}$ (kJ $\mathrm{mol^{-1}}$)	$\Delta S^{\neq}$ (J $\mathrm{K^{-1}\ mol^{-1}}$)
Non-isothermal				
Integral	125 ± 1^{a}	123 ± 3^{a}	94 ± 1^{c}	20 ± 3^{c}
	127 ± 1^{b}	130 ± 2^{b}	93 ± 1^{d}	18 ± 2^{d}
Differential	127 ± 1^{a}	128 ± 1^{a}	94 ± 1^{c}	22 ± 1^{c}
	124 ± 1^{b}	119 ± 1^{b}	91 ± 1^{d}	12 ± 1^{d}
Isothermal	130 ± 2	140 ± 6	89 ± 2	5 ± 6

$^{a}\lambda = 238$ nm. $^{b}\lambda = 263$ nm. $^{c}\alpha = 2.0$ K/min. $^{d}\alpha = 0.99$ K/min.

the temperature. The maximum of velocity, corresponding to the inflection point of the sigmoid, is followed by a smooth decrease of the rate until the end of the reaction. The rate constant at each point can be obtained dividing the first derivative by the normalized optical density $(D_t - D_\infty)$. Figure 1(f) shows the entire $k(T)$ profile.

The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ can be obtained in two alternative ways. The first one involves a direct best fitting of the experimental kinetic data, such as those in Fig. 1(d), to eqn. (10), using the PeakFit programme and the Romberg method of evaluating the integral present. The solid line in Fig. 1(d) is relative to the theoretical values. Alternatively it is possible to apply a linear or a non-linear fitting to the $k(T)$ profile. The solid circles in Fig. 1(f) refer to rate constants taken at constant temperature and used to calculate the activation parameters. An almost identical $k(T)$ profile is obtained by the two methods.

Table 1 lists the activation parameters for both reactions under study as obtained by applying the two processing methods (integral and differential) to the spectrophotometric non-isothermal kinetics. It can be seen that the values obtained by the non-isothermal method, using either the integral or the differential analysis, are almost identical and have very low statistical errors. These values are comparable with those obtained by the isothermal method, where the error is greater.

Conclusions

The non-isothermal kinetic method for unimolecular reactions offers a number of advantages for the treatment of kinetic data taken at various temperatures. (i) With a single kinetic run it is possible to obtain a $k(T)$ profile instead of a single rate constant. This saves time and chemicals. (ii) The whole set of data derives from a single experiment carried out in homogeneous conditions. (iii) The experimental data are obtained over a sufficiently large range of temperature and their number is very high so that the statistical error involved is significantly reduced.

For non-unimolecular reactions carried out under pseudo-first-order conditions (e.g. a nucleophilic substitution reaction of a square planar complex, where $k_{\mathrm{obs}} = k_1 + k_2[\mathrm{Y}]$) the $k(T)$ profile becomes the $k_{\mathrm{obs}}(T)$ profile and contains different contributions. In these cases it is necessary to perform the usual analysis of the dependence of k_{obs} on the concentration of all of the reagents that now can be made in the whole temperature range by a global fitting. A number of these cases are under investigation and will be published soon.

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