Variable-concentration Kinetics

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Just one kinetic run carried out at variable concentration of reactant is sufficient to determine the dependence of the pseudo-first-order rate constant of a reaction on the concentration of that reactant.

The quantitative investigation of the concentration dependence of a chemical reaction can take many days work.[1] However, using computer analysis, a new method has been developed which makes it possible to obtain the concentration dependence of the rate constant from a single kinetic run carried out under pseudo-first-order conditions. The method is quite general and it can be applied to most of the usual studies on reaction mechanisms of inorganic, organic and biological interest. Such a method is based on the fact that for a generic reaction [eqn. (1)] the general rate law is given by

$$\mathrm{A} \rightarrow \mathrm{B} \tag{1}$$

eqn. (2) where k is the rate constant, which depends on many

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = k(T, P, [Y_\mathrm{i}], \mu, \ldots)[A] \tag{2}$$

parameters such as the temperature, pressure, concentration of other reagents, ionic strength. When the reaction is carried out under pseudo-first-order conditions, all the values of these physical parameters are maintained constant, during the kinetic run. If a physical parameter changes during the course of the reaction, eqn. (2) maintains its validity but, under these circumstances, the rate depends on the product of two varying terms $[\mathrm{A}] = [\mathrm{A}](t)$ and $k_\mathrm{obs} = k_\mathrm{obs}[Par_i(t)]$, where $Par_i(t)$ is the parameter i varying with the time. This equation can be used in the differential form [eqn. (3)] by which it is possible to

$$-\frac{1}{[\mathrm{A}]}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \{k_\mathrm{obs}[Par_i(t)]\}_{Par \neq Par_i} \tag{3}$$

obtain the value of k_obs at each time of the kinetic, *i.e.* for each value of the physical parameter, if this is varied in a known way with time. When the mathematical form of the function $k_\mathrm{obs}[Par_i(t)]$ is known, the integral kinetic expression can be used for a direct best fitting of the experimental data [eqn. (4)] to obtain the optimized values of the terms regulating the dependence of the k_obs on that parameter.

$$[\mathrm{A}] = [\mathrm{A}]_0 \mathrm{e}^{-\int_0^t k_\mathrm{obs}[Par_i(t)]\,\mathrm{d}t} \tag{4}$$

Very recently[2] the dependence of a first-order rate constant on the temperature (and then the activation parameters $\Delta S^{\neq}$ and $\Delta H^{\neq}$) has been obtained spectrophotometrically in such a way using eqn. (3) in the form of eqn. (5).

$$\left|\frac{1}{D_\mathrm{t} - D_\infty}\frac{\mathrm{d}D_t}{\mathrm{d}t}\right| = \{k_\mathrm{obs}[T(t)]\}_{Par \neq T} \tag{5}$$

where D_t and D_∞ are the absorbances at time t and at the end of the reaction, respectively, and $T(t)$ is a linear function of the time as realized by means of a Perkin-Elmer peltier temperature programmer. Experimental data have also been analysed by a direct best fitting to the integral eqn. (6) with D_0 (the

$$D_\mathrm{t} = (D_0 - D_\infty)\,\mathrm{e}^{-\frac{k}{h}\mathrm{e}^{\left[\frac{\Delta S^{\neq}}{R}\right]}\int_0^t (T_0 + \alpha t)\mathrm{e}^{\left[-\frac{\Delta H^{\neq}}{R(T_0 + \alpha t)}\right]}\mathrm{d}t} + D_\infty \tag{6}$$

absorbance at the start of the reaction), D_∞, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ as the parameters to be optimized. In this case $k_\mathrm{obs}[Par_i(t)]$ is given by the Eyring equation. This experiment was reported as a particular application to inorganic and organometallic

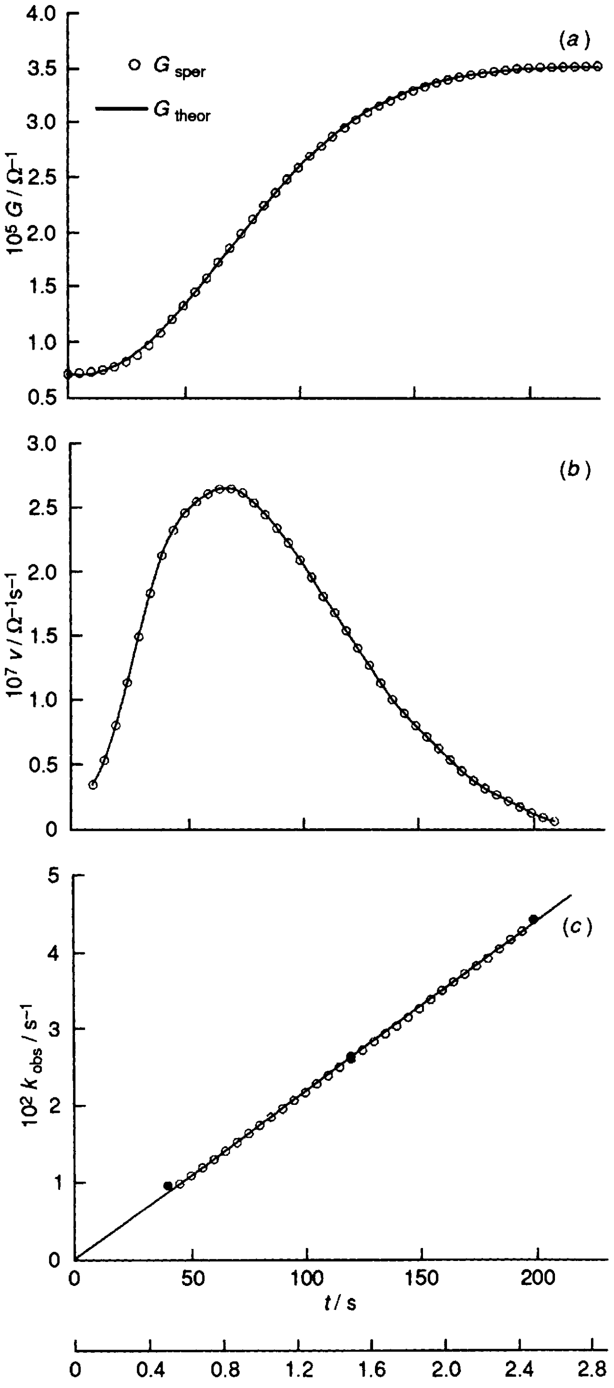

Fig. 1 (*a*) Change in conductance during the nucleophilic substitution of *trans*-$[\mathrm{Pt(PEt_3)_2Cl_2}]$ by thiourea to yield *trans*-$[\mathrm{Pt(PEt_3)_2Th_2}]^{2+}$ and $\mathrm{Cl^-}$ in MeOH, at 292.16 K, under a concentration gradient of thiourea $\gamma = 1.25 \times 10^{-5}$ mol dm^{-3} s^{-1}. Solid line is the theoretical curve in accordance to eqn. (9); (*b*) Trend of the rate of reaction as obtained by differentiation of the kinetic curve; (*c*) $k_\mathrm{obs}(C)$ profile as obtained by dividing the first derivative of the kinetic curve by $(G_\mathrm{t} - G_\infty)$. Solid line is for theoretical values. Solid circles are for kinetic runs carried out using the traditional constant concentration method.

reactions of non-isothermal kinetic analysis.[3] In the light of this new data, it can be inserted in a more general context of variable physical parameter kinetics.

Here attention has been focused on the study of the dependence of the rate constant on the concentration of a reagent. This kind of study usually requires a great deal of kinetic work but it is of major importance because it is mainly based on the formulation of the mechanistic scheme of the reaction under investigation.[1,4,5] A suitable system is the nucleophilic substitution of a square-planar complex that usually has a bimolecular mechanism with two parallel, solvolitic and nucleophilic, pathways and a mathematical form for the rate constant $k_{obs} = k_s + k_y\,[Y]$.[6] The reaction chosen was

$$trans\text{-}[Pt(PEt_3)_2Cl_2] + 2Th \rightarrow trans\text{-}[Pt(PEt_3)_2Th_2]^{2+} + 2Cl^- \quad (7)$$

the mechanism of which is well known and where the first substitution of chloride ion is the rate determining step, the second one being very fast.[7] It was carried out in a 25 ml thermostatted vessel, under vigorous magnetic stirring, using a conductometric cell and a conductometer connected to a microcomputer for the automatic collection of the conductance–time data. The variation of concentration of thiourea inside the vessel was ensured, following the relation $[Th] = \gamma t$, by a Radiometer ABU 12 autoburette, adding 2.5 µl s^{-1} (γ') of a 0.1 mol dm^{-3} solution of thiourea to 20 ml of 0.5×10^{-5} mol dm^{-3} solution of complex in MeOH. The concentration gradient was then $\gamma = \gamma'(M_{Th}/V_0) = 1.25 \times 10^{-5}$ mol $dm^{-3}\,s^{-1}$, with V_0 the starting reaction volume expressed in µl. The effect of dilution on the concentrations and on the rate of reaction was very low and not considered. The temperature was 292.16 ± 0.01 K.

The kinetic data were analysed by the same microcomputer both with the differential and integral methods. In the first one eqn. (8) has been used, where G_t and G_∞ are the conductance

$$\left|\frac{1}{G_t - G_\infty}\,\frac{dG_t}{dt}\right| = \{k_{obs}[[Th](t)]\}_{Par \neq [Th]} \quad (8)$$

at time t and at the end of the reaction, respectively, and $[Th](t)$ is a linear function of the concentration of thiourea with time. This form is particularly useful when a new system is under investigation since it gives information about the mathematical equation related to the observed rate constant. In the integral method eqn. (9) was used that is obtained

$$G_t = (G_0 - G_\infty)\,e^{\{-(k_S t + \frac{1}{2}k_{Th}\gamma t^2)\}} + G_\infty \quad (9)$$

replacing the term $k_{obs}[[Th](t)]$ by the relation $k_{obs} = k_S + k_{Th}[Th] = k_S + k_{Th}\gamma t$ into eqn. (8) and integrating.

Fig. 1(a) shows the change in conductance during the reaction that is accelerated in the first part due to the increase of the concentration of nucleophile and decelerated in the second part due to the overwhelming decrease of the concentration of complex. The Jandel Scientific PEAKFIT program was used to perform a direct best fitting to eqn. (9) with G_0 (the conductance at the start of reaction), G_∞, k_S and k_{Th} as the parameters to be optimized. The optimized values are† $k_s = (-1.20 \pm 0.14) \times 10^{-3}\,s^{-1}$ and $k_{Th} = 19.3 \pm 0.2\,dm^3\,mol^{-1}\,s^{-1}$, $r^2 = 0.9998$ [Fig. 1(a)]. Fig. 1(b) shows the trend of the rate of the reaction as obtained by deriving the kinetic curve by the Savitzky–Golay method.[8] Fig. 1(c) shows the trend of the observed rate constant [$k(C)$ profile] as obtained by dividing the first derivative to the normalized value of the conductance [eqn. (8)]. The points analysed were those where pseudo-first-order conditions were ensured. The dependence of k_{obs} on the concentration is typical for nucleophilic substitutions on square-planar complexes according to the rate law $k_{obs} = k_s + k_y[Y]$. The values obtained by a linear regression analysis are† $k_s = (1.87 \pm 0.12) \times 10^{-4}\,s^{-1}$ and $k_{Th} = 20.2 \pm 0.1\,dm^3\,mol^{-1}\,s^{-1}$. The values obtained from the experiments carried out at constant concentrations of thiourea are in accordance† [$k_s = (1.08 \pm 0.53) \times 10^{-4}\,s^{-1}$ and $k_{Th} = 19.6 \pm 0.4\,dm^3\,mol^{-1}\,s^{-1}$; Fig. 1($c$)].

The author is grateful to Professor Raffaello Romeo for many suggestions and thanks the Italian MURST and CNR for financial support.

Received, 2nd September 1994; Com. 4/05360E

Footnote

† k_S is too small with respect to k_{Th} so that it is not possible, in this case, to obtain it with good precision.

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