JOURNAL OF
Materials
CHEMISTRY

An approximate non-isothermal method to study kinetic processes controlled by a distribution of rate constants: the case of a photochromic azobenzene derivative dissolved in a polymer matrix

Krzysztof Janus,*[a] Igor A. Koshets,[b] Juliusz Sworakowski[a] and Stanislav Nešpůrek[c]

[a]*Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, 50-370 Wrocław, Poland*
[b]*Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kyiv 03028, Ukraine*
[c]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague, Czech Republic*

Received 31st October 2001, Accepted 26th March 2002

An approximate method is put forward allowing one to extract information on the parameters determining rate constants (activation energies and frequency factors) from non-isothermal measurements of quantities proportional to the concentrations of reactants (*e.g.*, absorbance). The method, based on an approximate solution of a first-order kinetic equation in a non-isothermal regime, has been extended to fractional-heating experiments—a technique often used to extract parameters of the distributions of rate constants. The method was employed to obtain information on the parameters controlling the thermally driven *cis–trans* isomerisation of a novel photochromic azobenzene derivative: azobenzene-containing crown ether dissolved in a polystyrene matrix. The kinetics of the thermal isomerisation is controlled by a distribution of rate constants, with the activation energy amounting to *ca.* 97 kJ mol^{-1} and the frequency factor of the order of 10^{10} s^{-1} The results obtained are in a good agreement with results of isothermal experiments performed on similar systems.

1 Introduction

Photoactive molecular materials have recently attracted much attention due to the increasing prospect of their use in modern technologies related to information processing and recording. Among them, photochromic materials occupy a prominent position.[1,2] A photochromic process can be defined as a reversible sequence of chemical reactions, the primary step ('forward' reaction) being photochemically driven, whereas the reverse reaction may be either a photochemical or a thermally driven process. The proper design of photochromic systems requires that individual reactions be correctly identified and the parameters controlling the process be properly determined. The rate constants of thermal processes and quantum yields of photochemical ones are among the fundamental parameters that characterize the photochemical activity of photochromic compounds.

Photochromic systems are most conveniently used either as solid solutions of photoactive molecules dissolved in neutral matrices or as systems in which the photoactive moieties are chemically attached to neutral polymer chains. In both cases, one should expect a distribution of the microenvironments of the reacting species. Since many photochromic reactions are space-demanding processes, the kinetics of the chemical reactions should depend not only on the nature of reacting species but also on their environment. Thus, one may expect a distribution of the reaction rates. This effect has indeed been observed, *e.g.*, in substituted azobenzenes.[3–5]

The kinetics of thermally driven chemical reactions may be conveniently studied by following the temporal evolution of the spectra of the reacting systems. The rate constants are in this case usually determined from isothermal measurements performed at several temperatures. It should be pointed out here that isothermal methods are often time-consuming and may become unreliable if the system under study undergoes uncontrolled side processes following excitation [*e.g.* irreversible photochemical ('fatigue') reactions in photochromic systems]. In this case, the multiple excitation may result in accumulation of impurities which make it impossible to obtain a reliable determination of the kinetic parameters. The isothermal methods can be sometimes supplemented with (or even replaced by) methods operating in a non-isothermal regime.[6,7] Thus, although isothermal methods are, in principle, more informative than non-isothermal ones, the advantage of the latter techniques consists in allowing one to gain similar kinetic information from a run (or a sequence of runs) following a single excitation, the latter feature becoming particularly important in the case of systems undergoing unwanted side processes.

The analysis of non-isothermal data, relatively simple for discrete values of the rate constants, becomes more complex in the case of distributed parameters. The problem is similar to that encountered earlier by researchers studying the dielectric and electrical properties of condensed phases.[7–10] Several methods elaborated, *e.g.*, to study dielectric relaxations in the time domain or electric currents due to a detrapping of charge carriers, may be successfully adopted to interpret the kinetics of chemical reactions. The main difference, however, is that the dielectric methods measure quantities proportional to time derivatives of basic variables (polarization, concentration of charge carriers, *etc.*), while the spectroscopic methods yield the concentration. The difference, less important in case of isothermal measurements, becomes significant in non-isothermal techniques.

In our previous papers,[5,11] we put forward an approximate method that allowed a direct determination of the activation

DOI: 10.1039/b109902g

energy from non-isothermal spectroscopic experiments. The use of the method (an outline of which will be briefly presented in the following section) was, however, limited only to processes controlled by a discrete rate constant. The aim of the present paper is to extend the method to the case of 'fractional heating'—a technique often employed to deconvolute kinetic processes controlled by distributions of rate constants.[8,10,12–15] The results of model calculations will be compared with those obtained by experiment: we shall use the results of measurements carried out on polymer films containing a photochromic azobenzene-containing crown ether.

2 Basic equations and results of calculations

2.1 Processes controlled by a discrete rate constant

In principle, the reactions of interest are processes approaching equilibrium which may be schematically written as

$$\mathrm{R} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{P}$$

where k_1 and k_{-1} stand for the rate constants of elementary processes. In many cases, the elementary processes follow first order kinetics, and thus the temporal change of the concentration of the reactant (n) can be described by the differential equation

$$\frac{dn}{dt} = -k_1 n + k_{-1} n_{\mathrm{P}}, \tag{1a}$$

where n_{P} stands for the concentration of the product. In the following, we shall limit ourselves to the case commonly encountered in practice: $k_1 \gg k_{-1}$. Eqn. (1a) will now read

$$\frac{dn}{dt} = -kn, \tag{1b}$$

where the index labelling the rate constant has been omitted for simplicity. If the process is controlled by a discrete rate constant then, under isothermal conditions, the decays of both the concentration and its time derivative are exponential

$$n = n_0 \exp(-kt), \tag{2a}$$

$$\frac{dn}{dt} = -kn_0 \exp(-kt), \tag{2b}$$

where n_0 is the initial concentration of the reactant. It is commonly assumed that the rate constant fulfils the Arrhenius law

$$k = v \exp\left(-\frac{E_{\mathrm{A}}}{RT}\right), \tag{3}$$

where E_{A} stands for the activation energy and v for the frequency (pre-exponential) factor.

To determine the kinetic parameters characterizing a reaction, *i.e.* its activation energy E_{A} and frequency factor v from isothermal measurements, one should carry out a series of measurements at several temperatures exciting the sample prior to each run. The procedure itself may be a source of errors if unwanted side reactions (photo-induced decomposition, *etc.*) occur in the sample. In this case, one may attempt to get the same information from a single run (or a series of runs following a single excitation) performed *on the same sample* with variable temperature. Most often, a linear heating rate is employed, *i.e.*

$$T = T_0 + \beta t, \tag{4}$$

with β standing for the heating rate. The temperature dependence of the concentration of the reactant will follow the equation

$$n = n_0 \exp\left(-\frac{v}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E_{\mathrm{A}}}{RT}\right) \mathrm{d}T\right). \tag{5}$$

The integral in eqn. (5) has no exact analytical solution but for $E_{\mathrm{A}} \gg RT$ and $T > T_0$ an approximate solution holds

$$n = n_0 \exp\left[-\frac{vRT^2}{\beta E_A} \exp\left(-\frac{E_{\mathrm{A}}}{RT}\right)\right]. \tag{6}$$

By taking the time derivative of eqn. (5), one arrives at the equation equivalent to that describing experiments performed under the thermally stimulated regime,[7,8,10] commonly employed *e.g.*, in dielectric physics

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -n_0 v \exp\left(-\frac{E_{\mathrm{A}}}{RT} - \frac{v}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E_{\mathrm{A}}}{RT}\right) \mathrm{d}T\right). \tag{7}$$

It should be realized that non-isothermal methods based on eqn. (7) measure quantities proportional to *time derivatives of the concentration*, whereas spectroscopic measurements yield the *concentrations* of the reactants. In principle, the time derivative can be calculated numerically: by making use of the Lambert–Beer law, it is straightforward to demonstrate that the time derivative of the concentration is proportional to the time derivative of the absorbance of the reactant or the product. The latter function, however, is very sensitive to experimental noise, thus the method may yield results of doubtful reliability in the case of noisy measurements. In these cases, the procedure described below (which allows one to obtain the activation energy directly from the temperature dependence of the concentration measured in a non-isothermal regime) may prove simpler and more reliable.

Let us define the function $Z(T)$ as

$$Z(T) = T^{-2} \ln\frac{n_0}{n}, \tag{8}$$

Combination of eqns. (6) and (8) yields

$$Z(T) = \frac{vR}{\beta E_{\mathrm{A}}} \exp\left(-\frac{E_{\mathrm{A}}}{RT}\right). \tag{9}$$

Thus, one should be able to get the activation energy from the rectilinear portion of the ln $Z(T)$ *vs.* $1/T$ dependence.

To test the reliability of the approximate method, we performed computer simulations. A set of pre-determined input parameters was used to calculate the $n(T)$ and $Z(T)$ dependences from eqns. (5) and (8), respectively. The latter dependence was then re-plotted in the Arrhenius co-ordinates. Exemplary results are shown in Fig. 1: as can be seen, for the input parameters employed, the $Z(T)$ function becomes rectilinear at *ca.* 15 K above the initial temperature. The activation energy, determined from the Arrhenius fit to the $Z(T)$ function, reproduces the input value to within an accuracy of better than 1%.

2.2. Processes controlled by distributed parameters

The use of simple methods to interpret kinetic processes controlled by distributions of rate constants leads inevitably to qualitative errors which can be, at least to some extent, eliminated by the use of appropriate experimental techniques. This problem will be first illustrated by the results of model calculations.

Two limiting cases can be envisaged (see, *e.g.*, ref. 9): a distribution of rate constants may be due either to a distribution of activation energies or to a distribution of pre-exponential factors. If elementary events are disconnected, then it is reasonable to assume that the distribution functions are

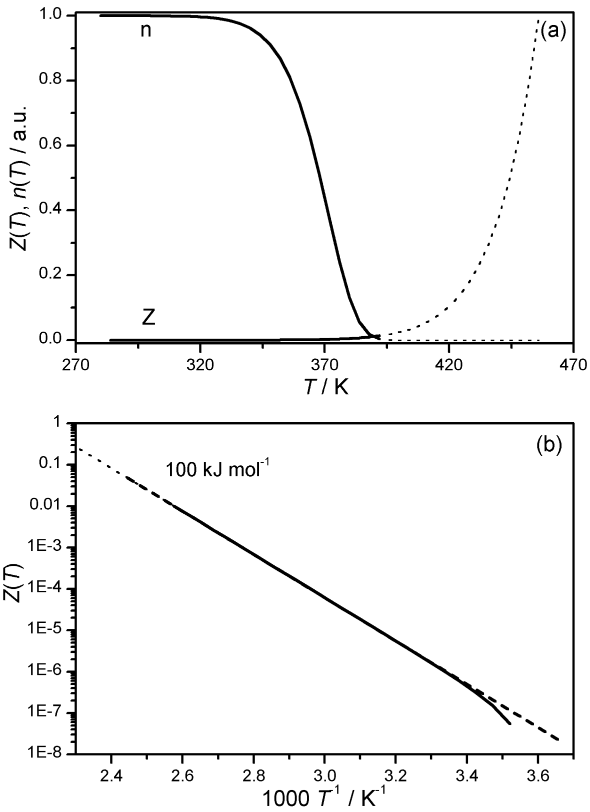

Fig. 1 (*a*) Temperature dependence of the concentration of the reactant species (*n*) and the corresponding $Z(T)$ function calculated for a process controlled by a discrete rate constant. The input parameters are: E_A = 100 kJ mol^{-1}, ν = 10^{12} s^{-1}, β = 0.1 K s^{-1}. The experimentally accessible ranges of values are marked with continuous lines (it was arbitrarily assumed that the concentration of the reactant can be monitored down to 3% of its initial value). (*b*) The Arrhenius plot of the $Z(T)$ function. Full line: experimentally accessible range of concentrations; dotted line: results of calculations beyond the experimentally accessible range; dashed line: a fit to the Arrhenius function. The output activation energy obtained from the fit is given in the figure.

Gaussian in shape. Thus, in the former case the input distribution of rate constants can be approximated by a single pre-exponential factor (ν) and a Gaussian distribution of activation energies centred at $E_{A,\max}$

$$n(E_A,t=0)=\frac{n_{\text{total}}}{\sigma_E\sqrt{2\pi}}\exp\left(-\frac{(E_A-E_{A,\max})^2}{2\sigma_E^2}\right), \quad (10a)$$

where $n_{\text{total}} = \int n(E_A,t = 0)\, dE_A$ is the initial total concentration of the reactant and σ_E stands for the variance of the Gaussian function, proportional to its width. In the latter case, the input distribution would be described by a single activation energy (E_A) and a Gaussian distribution of pre-exponential factors centred at ln $\nu_{\max}$

$$n(\ln\nu,t=0)=\frac{n_{\text{total}}}{\sigma_\nu\sqrt{2\pi}}\exp\left(-\frac{1}{2\sigma_\nu^2}\left(\ln\frac{\nu}{\nu_{\max}}\right)^2\right), \quad (10b)$$

where $n_{\text{total}} = \int n(\ln\nu,t = 0)\, d\ln\nu$.

The calculations presented in this paper will be limited to the case of distribution of activation energies. Fig. 2 shows results of calculations performed using a combination of eqns. (5) and (10a), mimicking a single-run non-isothermal experiment, with input parameters identical as those employed in the preceding section, except for the distribution of the activation energies. It is clearly seen that the shape of the $Z(T)$ function is in this case non-Arrhenius, and attempts to fit it to the Arrhenius function result in underestimated values of the activation energy.

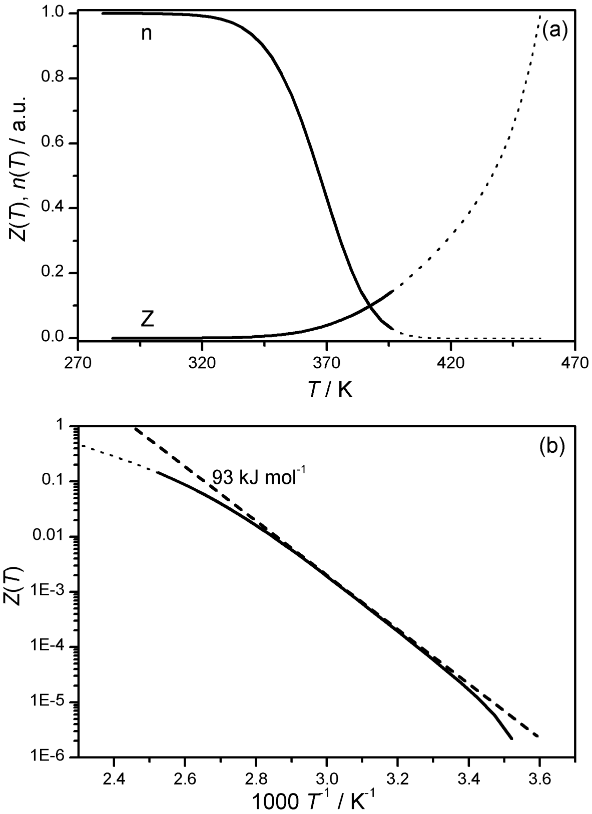

Fig. 2 (*a*) Temperature dependence of the concentration of reactant species and the corresponding $Z(T)$ function calculated for a process controlled by a distribution of the activation energies. The input parameters are: $E_{A,\max}$ = 100 kJ mol^{-1}, σ = 3 kJ mol^{-1}, other parameters as in Fig. 1. (*b*) The Arrhenius plot of the $Z(T)$ function. The dashed line is a fit to the middle section of the $Z(T)$ function.

A common way of deconvoluting processes controlled by a superposition of rate constants or by their distribution is the so-called 'fractional heating' method (sometimes also referred to as multi-stage[8] or peak-cleaning[14] method; see also ref. 10 and references cited therein). The method, the principle of which is illustrated in Fig. 3, consists in replacing a single heating run by a sequence of runs starting at a sufficiently low initial temperature and terminating at progressively increasing temperatures. If the elementary processes constituting the distribution are disconnected (*i.e.*, if an elementary act of reaction does not affect other reacting species), then the processes characterized by the largest rate constant (*i.e.*, by the lowest activation energy or the largest pre-exponential factor), will predominantly occur during the first thermal cycle, followed by slower ones occurring during the following cycles. The method, employed long ago in thermally stimulated luminescence and thermally stimulated current measurements[12,13] (see also Chap. 9 in ref. 7 and ref. 9), has recently been adopted in calorimetric measurements.[15–17] Here, we shall demonstrate its applicability to non-isothermal experiments in which the kinetics of a chemical reaction is monitored by measurements of optical absorbance.

The calculations performed using a combination of eqns. (5) and (10a) were aimed at mimicking fractional heating experiments. The results obtained for several widths of the distributions of the activation energies are shown in Fig. 4.

In the case of a kinetic process controlled by a discrete rate constant, all $Z(T)$ functions obtained for successive fractional runs are superimposed on one another (*cf.* Fig. 4a), whereas the presence of a distribution of rate constants (even of a relatively narrow one, σ = 1 kJ mol^{-1}) manifests itself by a relative displacement of the fractional curves (*cf.* Figs. 4b–d). Our calculations point to an interesting result: in the case of

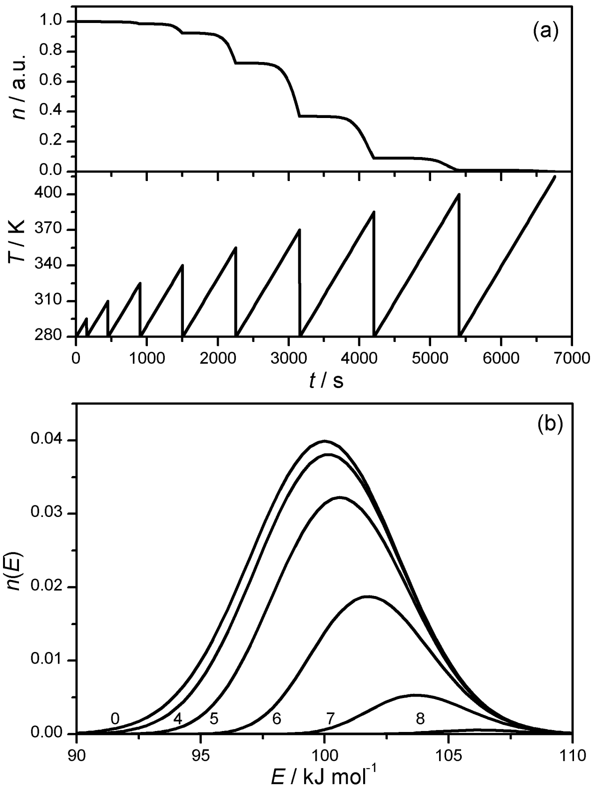

Fig. 3 The principle of a fractional-heating experiment. (*a*) A typical time–temperature ramp (lower section) and the corresponding temporal evolution of the reactant concentration (upper section). (*b*) Initial distribution of reacting species (the curve labelled '0') and distributions of reactants remaining after an *n*-th run. The data shown in the figure have been calculated for $E_{A,max}$ = 100 kJ mol^{-1}, σ = 3 kJ mol^{-1}, ν = 10^{12} s^{-1}, β = 0.1 K s^{-1}.

distributions of rate constants resulting from distributions of activation energies and a discrete pre-exponential factor, Arrhenius fits to the $Z(T)$ functions, calculated for successive fractional-heating runs, should nearly converge at $1/T \rightarrow 0$; note that such behaviour may be deduced from eqn. (9).

A similar analysis may also be performed for a distribution of rate constants resulting from a distribution of pre-exponential factors. Results of detailed calculations will not be presented here, but one can deduce, however, from eqn. (9) that in the case of such a distribution, Arrhenius fits to the $Z(T)$ functions obtained for successive fractional-heating runs should yield parallel rectilinear sections displaced with respect to one another. Thus, use of the fractional heating method should, in principle, allow one to extract information on the parameters that characterize a distribution of rate constants. The slopes of the rectilinear portions of the curves or their displacement should provide qualitative information about the widths of distributions, although the shape of the distribution cannot be quantitatively reproduced. In practice, however, distinguishing between the two distributions may be difficult due to a limited temperature range and insufficient accuracy of measurements, as will be shown in Section 3.

3 Experimental results

The calculations described in the preceding section will be compared with results of measurements performed on an azobenzene-containing 16-membered crown ether (hereafter referred to as O4N2—see Fig. 5). Crown ethers have been studied for many years due to their ability to complex metal ions.[18] Like the parent (unsubstituted) azobenzene, azobenzene-containing crown ethers undergo a reversible isomerisation between the stable *trans* and the metastable *cis* forms, the forward (*trans–cis*) reaction occurring upon illumination in the UV absorption band of the *trans* form, and the reverse process

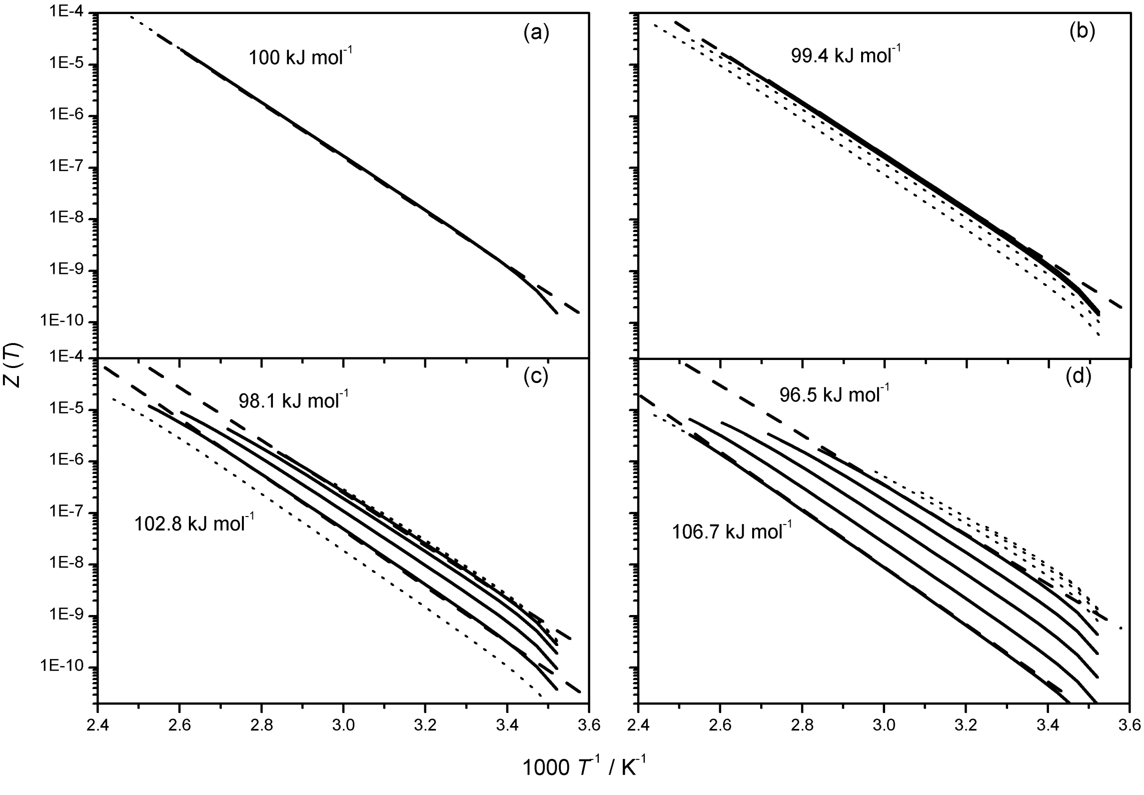

Fig. 4 Arrhenius plots of the $Z(T)$ functions calculated for processes controlled by distributions of the rate constants characterized by $E_{A,max}$ = 100 kJ mol^{-1}, ν = 10^{12} s^{-1}, β = 0.1 K s^{-1}. The widths of the activation energy distributions (σ) are 0 (discrete rate constant), 1, 3 and 5 kJ mol^{-1} for the plots (*a*)–(*d*), respectively. Full lines: experimentally accessible range of concentration; dotted lines: results of calculations beyond the experimentally accessible range; dashed lines: fits to the Arrhenius function. The numbers in the figures are the output activation energies determined from the fits to the first and last fractional runs.

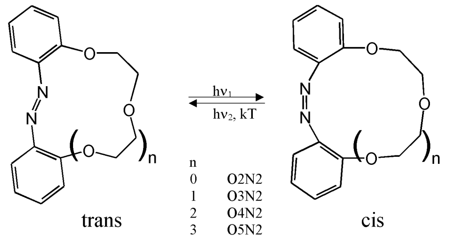

Fig. 5 *trans–cis* Isomerisation in azobenzene-containing crown ethers.

being driven thermally or by light. Earlier research performed by the present authors on 10-, 13-, 16-, and 19-membered crown ethers[3–5] (hereafter referred to as O2N2, O3N2, O4N2 and O5N2—*cf.* Fig. 5) demonstrated that in certain polymers a dispersion of the rate constants of the thermally driven *cis–trans* isomerisation was observed. The dispersion was interpreted as being due to a distribution of the activation energies, although the activation energy at the distribution maximum was found to be nearly independent of the matrix used.

The measurements reported in this paper were performed on samples containing O4N2 dissolved in polystyrene. The choice of the polymer matrix was motivated by the results of earlier experiments performed in the isothermal regime,[3,4] pointing to the existence of a distribution of rate constants. Details of the synthesis and purification of the crown ether are presented in ref. 19. A solution of the crown ether and the polymer in toluene was cast on glass plates and allowed to dry over several days at ambient temperature. Samples prepared in such a way were ~50 to ~150 μm thick, with concentrations of O4N2 in polystyrene being of the order of 0.1 to 1% (w/w).

Absorption spectra were measured with a Perkin Elmer Lambda 20 spectrophotometer equipped with a Peltier thermostat and an additional thermometer to collect the temperature data during the experiments. The irradiation of as-received samples or thermally treated samples was performed inside the spectrophotometer chamber using a 200 W mercury lamp with a water filter and appropriate combination of colour filters transmitting light at 365 nm, shining into the π–π* absorption band of the stable (*trans*) form of the azobenzene moiety. A silica optical fibre was used to deliver light to the samples. The irradiation resulted in the photochemical *trans–cis* reaction; the kinetic process studied in the present paper was the reverse (*cis–trans*) reaction.

Fig. 6a shows the absorption spectra of a thermally treated sample, and the spectrum of the same sample after irradiation into the π–π* absorption band of azobenzene. The former spectrum is that of a sample containing mostly the *trans* isomer, the irradiation resulting in the *trans–cis* photoisomerization. The amount of the *cis* isomer can be estimated by comparing the spectrum of an irradiated sample with that of the pure *cis* isomer. The latter spectrum can be calculated using the Fischer method;[20] the calculations performed for a di-*tert*-butyl derivative of O4N2 have been reported in ref. 21. A comparison of the extrapolated spectrum with that shown in Fig. 6a allows one to calculate the fraction of the *trans* isomer in irradiated samples to amount to *ca.* 15% of the total. It should be stressed, however, that in the experiments reported in this paper we did not attempt to attain photostationary states during UV irradiation of the samples under study.

The results of a typical isothermal kinetic experiment are shown in Fig. 6b. The kinetics was measured by monitoring the temporal evolution of the absorption at 355 nm; the latter dependence can be transformed into the temporal evolution of the concentration of the reactant using the Lambert–Beer law

$$\frac{n}{n_0}=\frac{A_{\mathrm{inf}}-A}{A_{\mathrm{inf}}-A_0}, \qquad (11)$$

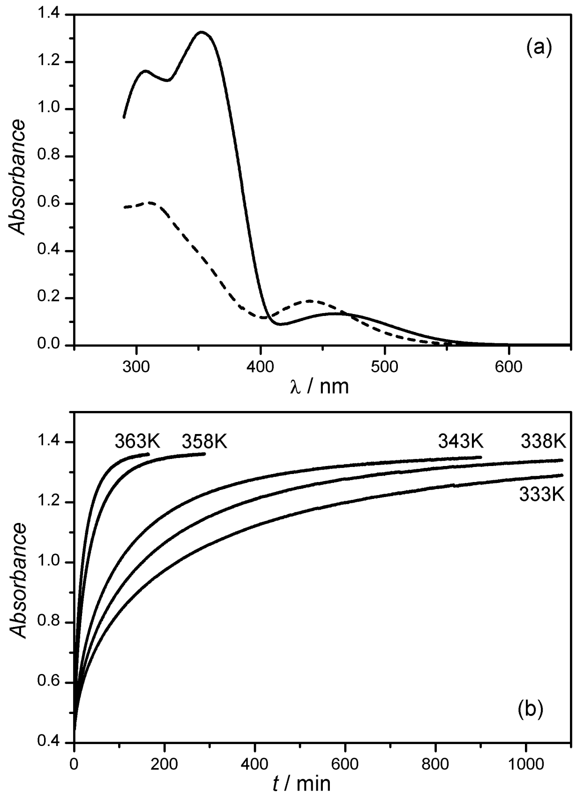

Fig. 6 (*a*) Absorption spectrum of O4N2 in polystyrene matrix. Full line: a thermally treated sample, containing mostly the *trans* isomer; dashed line: the sample illuminated with UV light (λ = 365 nm), containing mostly the *cis* isomer. (*b*) Temporal evolution of the absorbance at 355 nm measured at several temperatures indicated in the figure.

where A stands for the momentary absorbance, and A_{inf} and A_0 for the absorbances at $t = \infty$ and $t = 0$, respectively. As is shown in Fig. 7, the decay is clearly non-exponential although the reaction has been known to be a first-order process. It is worth noting that the curves are well fitted with the KWW ('stretched exponential') function

$$n=n_0\exp\left(-(k_{\mathrm{KWW}}t)^{\beta}\right), \qquad (12)$$

where β is a time-independent parameter ($\beta < 1$). The KWW fit to the curves is shown in Fig. 7a. The activation energy E_{KWW}, determined from the temperature dependence of k_{KWW}, was found to be equal to 87 kJ mol^{-1}.

The results of earlier isothermal experiments[4,5] performed on O4N2 in polystyrene were interpreted by assuming that the kinetics of the thermal *cis–trans* isomerisation is controlled by a distribution of rate constants, associated with a distribution of activation energies [eqn. (10a)] peaking at 95 kJ mol^{-1}, with $\sigma_E \approx 3$ kJ mol^{-1} (average values from several samples). The curves shown in Fig. 7 can be fitted with $E_{\mathrm{A,max}}$ = 91 kJ mol^{-1}, σ_E = 2.45 kJ mol^{-1}, ln ν = 23.1 (see Fig. 7b); it should be pointed out, however, that a reasonable fit to the experimental results can be achieved assuming a distribution of frequency factors [eqn. (10b)]: the parameters of the fit, shown in Fig. 7c, are: E_{A} = 91 kJ mol^{-1}, ln ν_{max} = 23.1, σ_{ν} = 0.85.

The results of non-isothermal experiments performed on the same system are shown in Figs. 8 and 9. A single-run experiment is shown in Fig. 8. The slope of the $Z(T)$ function yields the apparent activation energy (E_{app}) equal to 55 kJ mol^{-1}, obviously underestimated, similar to the outcome in our earlier papers reporting the results for the O4N2–pMMA system.[3–5] It was demonstrated (*e.g.*, ref. 8, Chap. 2.2.5a) that such an effect should be encountered in the case of

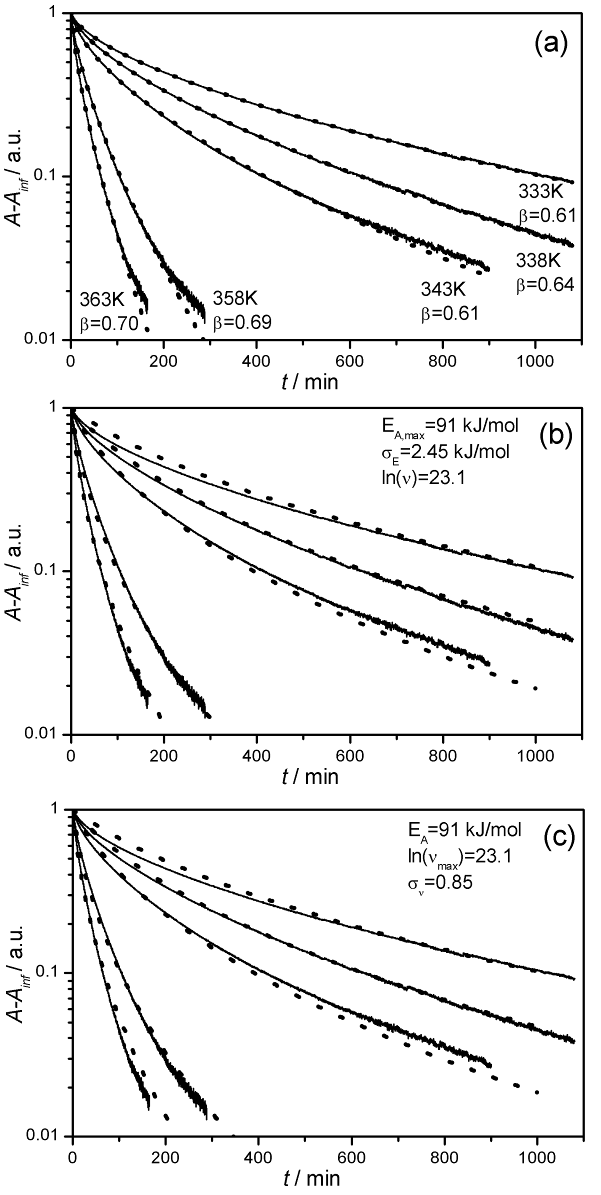

Fig. 7 Temporal evolution of the concentration of the *cis* form of O4N2 calculated from the data of Fig. 6b using eqn. (11). The fits to the experimental results were calculated using the KWW function (a), and assuming a distribution of activation energies (b) and a distribution of pre-exponential factors (c). The parameters of the distributions obtained from the fits are given in the figures.

distributions of kinetic parameters: in this case the ratio $E_{\mathrm{app}}/E_{\mathrm{KWW}}$ should be equal to β. A comparison of the respective activation energies with the values of β shown in Fig. 7a demonstrates that an approximate equality is indeed fulfilled.

More correct values can be obtained from fractional-run experiments: the results presented in Fig. 9 can be interpreted as being due to a distribution of activation energies ranging between *ca.* 95 and 100 kJ mol^{-1}, although the lower limit could only be roughly estimated due to the insufficient extent of the straight-line portions of the $Z(T)$ functions determined from the few first fractional runs. It should be noted that the accuracy of the determination does not allow us to discriminate unequivocally between the distribution of activation energies and a distribution of pre-exponential factors: the experimental results can also be interpreted in terms of a process characterized by an activation energy amounting to 99 kJ mol^{-1} and a distribution of pre-exponential factors, the values of ln ν ranging between *ca.* 21.7 and 23.2.

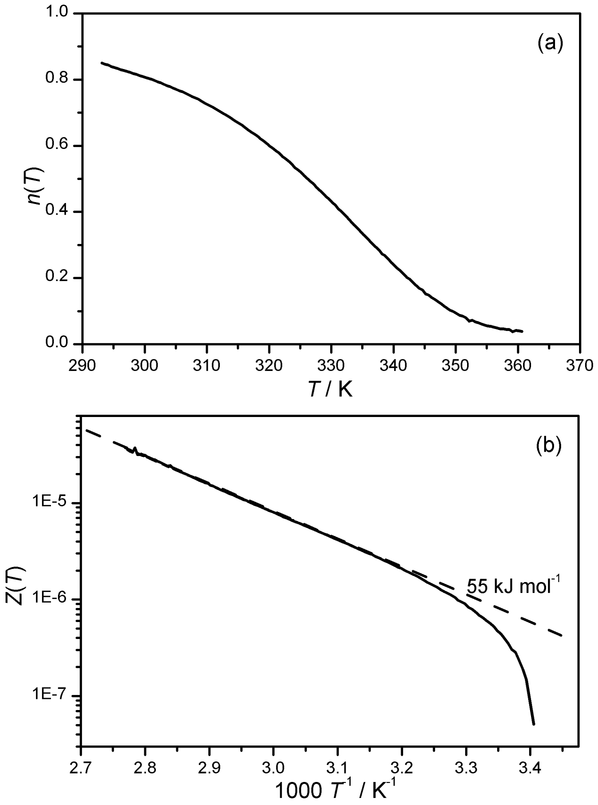

Fig. 8 A single-run non-isothermal experiment performed on O4N2 in polystyrene matrix. (*a*) Temperature dependence of the concentration of reactant species calculated from the temperature dependence of the absorbance at 355 nm. (*b*) The corresponding $Z(T)$ function.

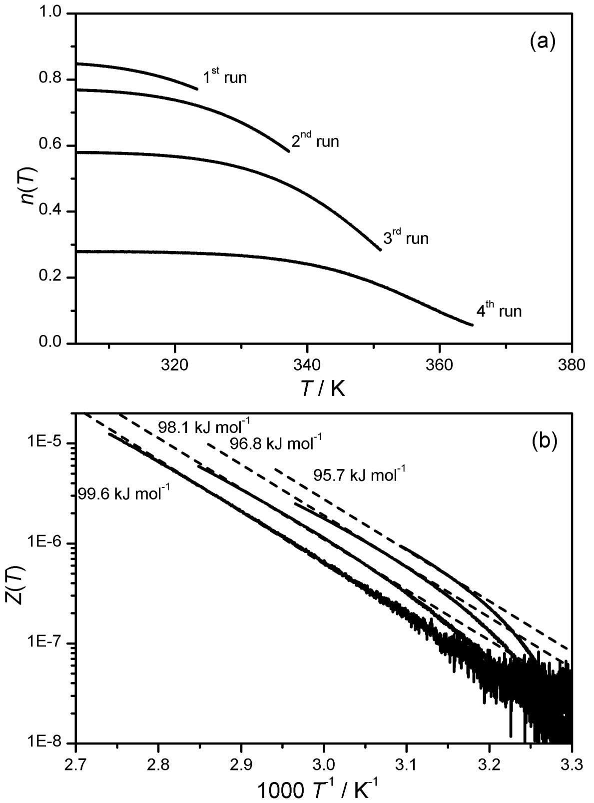

Fig. 9 Fractional-run experiments performed on O4N2 in polystyrene matrix. (*a*) Temperature dependence of the concentration of reactant species calculated from the temperature dependence of the absorbance at 355 nm. (*b*) The corresponding $Z(T)$ function.

4 Final remarks

The main aim of the paper was to put forward an approximate method of interpreting non-isothermal kinetic experiments. The numerical simulations presented in Section 3 confirm the applicability of the method. For processes controlled by discrete rate constants or by narrow distributions, the activation energies can be reproduced to within 1% error. The accuracy is worse in the case of broader distributions but in all cases reliable results can be extracted from the temperature dependences of the reactant concentrations. The method may prove particularly useful in measurements performed on systems in which a multiple excitation may result in uncontrolled side reactions, and in which non-isothermal measurements are burdened with experimental noise. The method put forward in this paper also has its limitations: the approximate solution given by eqn. (6) holds only at temperatures sufficiently far above the starting temperature (10–15 K at least), thus the experimentally accessible temperature range should be at least twice as wide.

The experiments presented in this paper aimed only at illustrating the use of the method. The results obtained on a photochromic crown ether dissolved in a polystyrene matrix show that the kinetics of the thermally driven *cis–trans* isomerisation is controlled by a distribution of rate constants. In principle, the method described in the paper should allow us to decide whether the distribution of rate constants results from a distribution of activation energies or a distribution of pre-exponential factors; the limited temperature range covered by our experiments and the insufficient accuracy of the measurements does not allow us to discriminate between the two limiting cases.

Acknowledgement

The authors thank Dr Elżbieta Luboch (Technical University of Gdańsk) for the gift of O4N2 used in the measurements reported in this paper. The work reported in this paper was supported by the Polish State Committee for Scientific Research (KJ - Grant No 3 T09A 144 19), the Wrocław University of Technology (JS), and by the Grant Agency of the Academy of Sciences of the Czech Republic and the Grant Agency of the Czech Republic (SN - grants No A1050901 and 202/01/0518). The computational work was initiated while one of the authors (IAK) participated in the UNESCO course for PhD students supported by the Institute of Macromolecular Chemistry of the Academy of Science of the Czech Republic, UNESCO and IUPAC.

References

1 H. Dürr and H. Bouas-Laurent (Eds.), *Photochromism. Molecules and Systems*, Elsevier, Amsterdam, 1990.
2 J. C. Crano and R. J. Guglielmetti (Eds.), *Organic Photochromic and Thermochromic Compounds*, Plenum, New York, 1999.
3 K. Janus, J. Sworakowski, A. Olszowski, A. Lewanowicz, J. Lipiński, E. Lubicz and J. F. Biernat, *Adv. Mater. Opt. Electron.*, 1999, **9**, 181.
4 K. Janus, K. Matczyszyn, J. Sworakowski, J. F. Biernat and Z. Galewski, *Mol. Cryst. Liq. Cryst.*, 2001, **361**, 143.
5 J. Sworakowski, K. Janus and S. Nešpůrek, *IEEE Trans. Dielectr. Electr. Insul.*, 2001, **8**, 543.
6 E. Koch, *Non-Isothermal Reaction Analysis*, Academic Press, London, 1977.
7 R. Chen and Y. Kirsh, *Analysis of Thermally Stimulated Processes*, Pergamon Press, Oxford, 1981.
8 J. Van Turnhout, *Thermally Stimulated Discharge of Polymer Electrets*, Elsevier, Amsterdam, 1975.
9 N. G. McCrum, B. E. Read and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, London, 1967, Chap. 4.2.
10 G. Teyssedre, S. Mezghani, A. Bernes, C. Lacabanne, Thermally stimulated currents in polymers, in J. P. Runt and J. J. Fitzgerald (Eds.), *Dielectric Spectroscopy of Polymeric Materials. Funamentals and Applications*, American Chem. Soc., Washington DC, 1997, pp. 227–258.
11 K. Janus, J. Sworakowski and E. Luboch, *Chem. Phys.*, 2002, in the press.
12 J. Nahum and A. Halperin, *J. Phys. Chem. Solids*, 1963, **24**, 823.
13 H. Gobrecht and D. Hofmann, *J. Phys. Chem. Solids*, 1966, **27**, 509.
14 J. Vanderschueren and J. Gasiot, Field-induced thermally stimulated currents, in P. Bräunlich (Ed.), *Thermally Stimulated Relaxation in Solids*, Springer, Berlin, 1979, pp. 135–223.
15 J. Sworakowski and S. Nešpůrek, *Chem. Phys.*, 1998, **238**, 343.
16 A. Lewanowicz, J. Lipiński, S. Nešpůrek, A. Olszowski, E. Śliwińska and J. Sworakowski, *J. Photochem. Photobiol. A*, 1999, **121**, 125.
17 E. Śliwińska and J. Sworakowski, *Adv. Mater. Opt. Electron.*, 1999, **9**, 167.
18 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.
19 J. F. Biernat, E. Luboch, A. Cygan, Y. A. Simonov, A. A. Dvorkin, E. Muszalska and R. Bilewicz, *Tetrahedron*, 1992, **48**, 4399.
20 E. Fisher, *J. Phys. Chem.*, 1967, **71**, 3704.
21 I. Zawisza, R. Bilewicz, K. Janus, J. Sworakowski, E. Luboch and J. F. Biernat, *Mater. Sci. Eng., C*, 2002, **19**, in the press.