Isothermal and Non-Isothermal Techniques in Kinetic Studies of Reactions in a Photoactive Molecular Material

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Abstract. The kinetics of thermally driven reactions in a crystalline photochromic solid, 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (DHP), has been studied. The processes have been monitored by measuring the isothermal bleaching of coloured species produced upon UV irradiation of DHP, and by measuring the heat flow in non-isothermal differential scanning calorimetry experiments. Signatures of two processes were detected; a combination of quantum-chemical calculations and spectroscopic measurements allowed us to attribute them to reactions occurring in the photochromic system.

Key words: dihydropyridine, photochromism, kinetics.

1. Introduction

Although photoactive properties of several molecular systems have been known for decades [1, 2], recent years have brought a revival of interest in these systems due to their potential use as components of information-processing media [3, 4]. In most cases, photochromic reactions (i.e., reversible reactions in which at least one stage – the 'forward reaction' – is photochemically driven) involve important rearrangement of molecular structures, one may therefore expect them to be strongly environment-dependent. This feature is likely to strongly influence the kinetics of such processes occurring in the solid state, where one may expect the existence of a distribution of microenvironments of reactive species, associated with defects, mesoscopic-scale inhomogeneities, etc. For practical purposes, photoactive species are most often used in the form of solid samples (polycrystalline materials or solid solutions). Thus, a reliable and simple determination of parameters characterizing the kinetics of reactions in such systems seems to be a matter of importance.

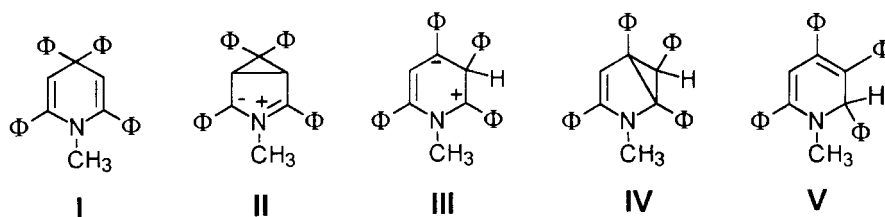⋆ Author for correspondence. E-mail: sworakowski@kchf.ch.pwr.wroc.pl

Figure 1. Chemical formulae of the stable form (I) of DHP, and of a few postulated products of photochemical reactions.

The main aim of this paper is to demonstrate the application of straightforward methods of analysis of isothermal and non-isothermal kinetics of thermally driven reactions in a crystalline photochromic solid 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (hereafter referred to as DHP, structure I in Figure 1). The compound under investigation belongs to a relatively poorly known family of photoactive compounds, previously studied by Japanese [5], Czech [6, 7], and Iranian [8, 9] groups. The stable form of DHP is transparent in the visible region, the long-wavelength edge of the absorption being located at ca. 370 nm; upon illumination into the UV absorption band, a coloured form appears, with the absorption band centred around 560 nm, which can then be bleached thermally [6].

The mechanism of the photochemical activity of DHP and related compounds has been subject to some dispute [5–9]: essentially, two possible mechanisms have been postulated to account for the existence of the photochromic cycle: (i) a 3–5 bridge formation and ring closing (**I** ⇔ **II**, cf. the molecular structures depicted in Figure 1), or (ii) an intramolecular phenyl shift (**I** ⇔ **III**). Moreover, some further processes have also been proposed, leading to other products shown in Figure 1 [5–9].

2. Experimental

Polycrystalline samples of DHP were obtained from Prof. J. Kuthan and Dr S. Böhm (Prague Institute of Chemical Technology). The synthesis and purification of the material have been described elsewhere [6].

The isothermal kinetics of the bleaching reaction was determined spectrophotometrically, by measuring the temporal evolution of the 560 nm band detected either in the reflection spectra of DHP/MgO mixtures, or in the absorption spectra of polycrystalline DHP in KBr matrices. The non-isothermal kinetics was measured using differential scanning calorimetry (DSC). Taking into account a possible distribution of rate constants controlling the kinetics of thermally-driven reactions, we employed the technique of Fractional Heating DSC [10].
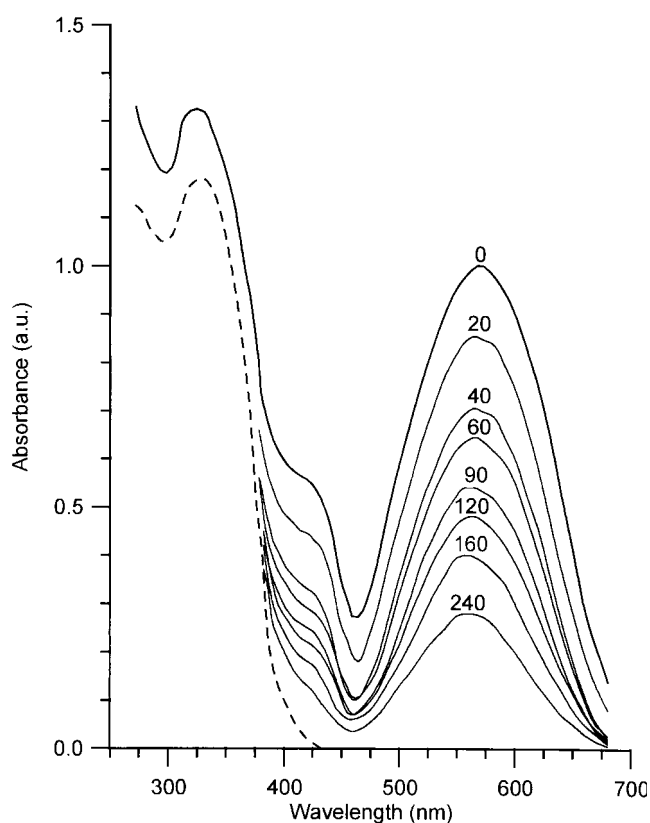
Figure 2. Absorption spectra of the stable form of DHP (broken line) and the coloured form (solid lines). The spectra have been calculated from the reflection spectra of the DHP/MgO mixtures using the Munk-Kubelka method. The curve labelled "0" was measured on a sample previously irradiated with UV, directly after the exposure, other curves refer to measurements taken during the thermal bleaching of the sample at ambient temperature; the parameter is the bleaching time (in minutes).

3. Results and Discussion

The spectra of the stable and coloured forms of DHP are shown in Figure 2. As is clearly demonstrated in the figure, changes of the concentration of the coloured form can be followed by monitoring the temporal evolution of the band centred at ca. 560 nm. Figure 3 shows results of measurements of the isothermal kinetics of bleaching of a polycrystalline DHP/MgO sample measured in such a way. Although independent measurements performed on chloroform solutions of DHP [11] have demonstrated that the reaction is of the first order, the decays shown in Figure 3a are clearly non-exponential, being instead well fitted by the 'stretched-exponential' equation
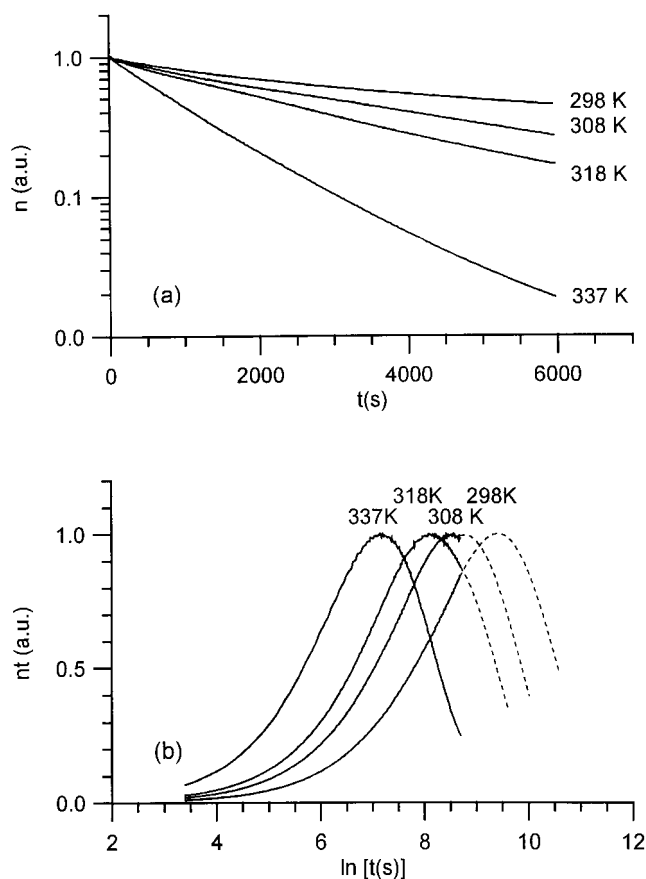
Figure 3. The isothermal kinetics of the bleaching reaction in polycrystalline DHP meas-
ured by following the absorbance of a poly-crystalline sample at 560 nm. (a) "Conventional"
semi-logarithmic plots parametric in temperature, normalized to their initial values. (b) The
curves from (a) re-plotted in the new co-ordinates and normalized at their peak values.

$$n(t) = n(0) \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \tag{1}$$

with n standing for the concentration of the reactant, τ for a time constant, and β
for a time-independent parameter ($0 < \beta \leq 1$). This feature can be interpreted
as due to a distribution of rate constants controlling the reaction in the solid state.
According to Richert and Bässler [12, 13], such a distribution may translate into a
Gaussian distribution of activation energies.

In our previous paper [14], we put forward a method of analysis of non-
exponential decays allowing us to extract in a straightforward way information
concerning the position of the maximum and the width of the distribution of the
activation energies. The method consists in analysis of the decays re-plotted in the
$[t \times n(t)$ vs. $\ln t]$ co-ordinates: the maximum of the curve obtained in such a way is

related to the position of the maximum of the distribution, whereas its width contains information about the distribution width. The results of Figure 3a, re-plotted in the new co-ordinates and displayed in Figure 3b, can be well fitted with three temperature-independent parameters: the energy of the distribution maximum E_m = 41.1 kJ/mol, the dispersion of the Gaussian function σ = 2.3 kJ/mol (translating into the distribution width FWHM = 5.3 kJ/mol), and the pre-exponential factor in the Arrhenius equation $A = 2 \times 10^3$ s^{-1}.

It should, however, be pointed out that isothermal measurements are often time-consuming; moreover, in some samples, due to the influence of unwanted side processes, performing a series of reliable measurements may become a problem. Difficulties of this type can be overcome by using a thermally stimulated (non-isothermal) technique. The method essentially consists in measuring a kinetic response of a sample upon linearly increasing the temperature. A good example of the method is the DSC technique, which was employed to study the reaction in polycrystalline DHP samples [10, 15]. DSC runs performed on DHP samples, UV-irradiated to produce the coloured product, exhibit the presence of a broad exothermic anomaly peaking around 330–350 K, observed only once after irradiation, and attributed to an exothermic reaction involving the metastable coloured species. Bearing in mind the results of the isothermal measurements reported above, which indicated the presence of a distribution of rate constants, we employed Fractional Heating DSC [10], allowing in principle to gather information about a distribution of activation energies. The latter technique consists of a sequence of heating runs to successively increasing temperatures (cf. Figure 4a); the slopes of the measured responses carry information about the activation energies and their distribution. Typical experimental results are shown in Figure 4b. We found that the activation energies determined from the Arrhenius fits to the experimental curves are burdened with a substantial spread thus the temperature dependence of the activation energy could not be reliably determined. The average value obtained from measurements performed on several samples was found to amount to (130 $\pm$ 30) kJ/mol. It should be noted that, in spite of a considerable spread of the results, the latter value significantly exceeds the activation energy determined from the isothermal measurements, and the difference cannot be attributed to any systematic error resulting from the use of different techniques.

Quantum-chemical calculations performed using the MNDO [16] and GRINDOL [17] methods (reported in detail elsewhere [18]), combined with spectroscopic measurements, allowed us to propose a scheme explaining the reversible (photochromic) and irreversible photochemical and thermally-driven processes occurring in DHP (Figure 5). According to the model, irradiation within the absorption band of the stable form of DHP (**I** in Figure 1) results in production of the coloured form **III**, which then can decay thermally to the forms **IV** and **V**, non-absorbing in the visible but having absorption bands in the near UV, close to that of the stable form (the form **V** is an analogue of one of the compounds postulated for a thiopyran analogue of DHP [8, 9]). A subsequent UV irradiation
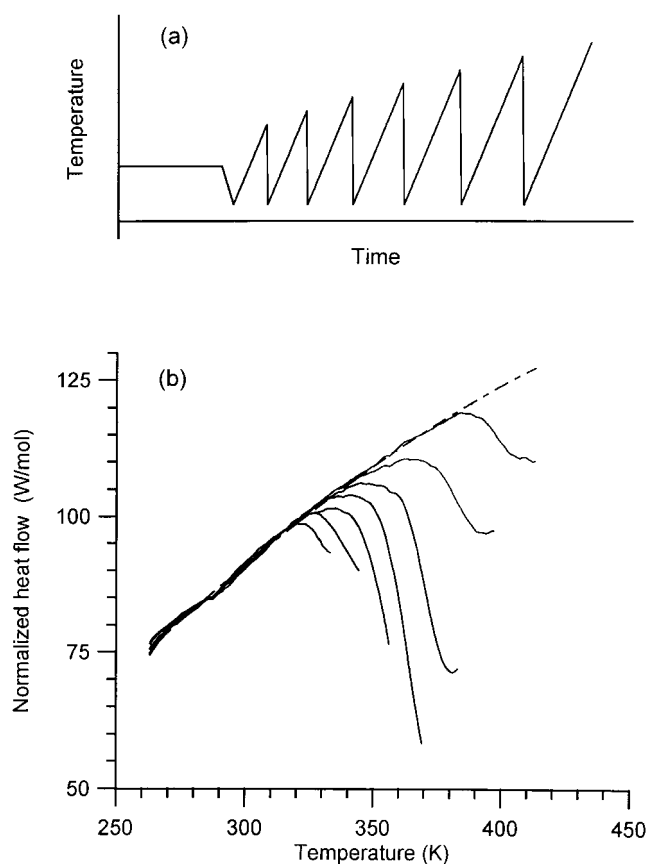
Figure 4. Fractional Heating DSC. (a) A scheme of the temperature programme during a typical run; the reactive form is produced by irradiating the stable form at ambient temperature (the period corresponding to the horizontal section of the diagram). (b) Experimental curves measured on a poly-crystalline DHP sample.

of the sample containing **IV** may either reproduce the product **III** or may give rise to an irreversible reaction to a final (unidentified) product. The irradiation of **V** may also result in producing the coloured form **III** but the process is less probable in view of an energy barrier existing between the excited forms of **III** and **V**. The latter compound also may undergo a thermal reaction to a final product. The proposed mechanism accounts well for the difference of the activation energies reported above: use of two different techniques results in detecting signatures of *two different* processes. It should be pointed out that the experimentally determined activation energies appear in a reasonable agreement with the barrier heights calculated using quantum-chemical methods.
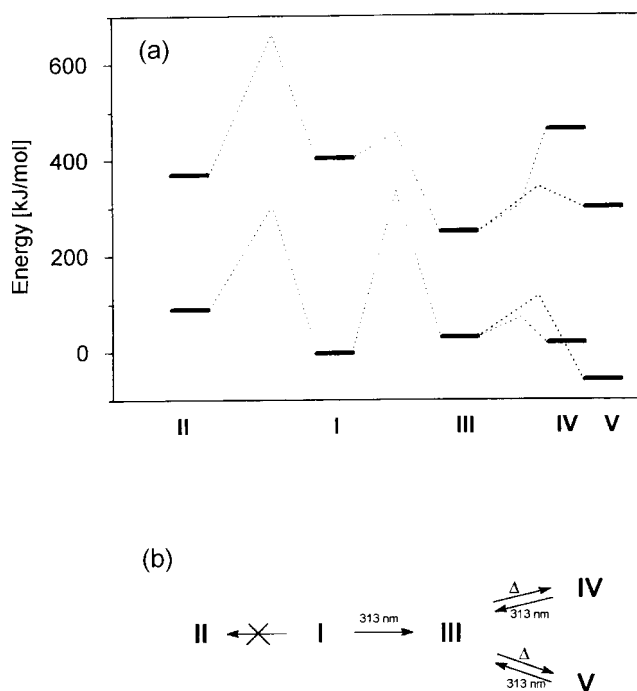
Figure 5. (a) Calculated energies of the ground and the lowest excited singlet states of the stable form of DHP, of the products shown in Figure 1, and of transition states between the reagents. The calculations were performed using the MNDO and GRINDOL methods [16–18]. Thick horizontal sections symbolize the energies of the molecules **I–V**, maxima of the broken lines correspond the energies of transition species. (b) The postulated reaction scheme. The numbers refer to the formulae shown in Figure 1.

4. Conclusions

We have studied the kinetics of thermally driven reactions in polycrystalline photoactive DHP using isothermal and non-isothermal methods (spectrophotometric measurements and differential scanning calorimetry, respectively). We found that in fact we observed signatures of two processes. A comparison of our experimental results with quantum-chemical calculations allowed us to identify the processes and put forward a mechanism for the photochemical activity of DHP. The kinetics of at least one of the reactions is controlled by a distribution of rate constants.

Acknowledgements

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