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Photochromic activity of dihydropyridine derivatives: energetics and kinetics of photochemically driven reactions in polycrystalline 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropydridine

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Abstract

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. The model put forward in the paper assumes that the primary photochemically driven reaction (intramolecular phenyl shift) is irreversible; the photochromic cycle consists of two parallel processes: 2,4-ring closing and intramolecular hydrogen shift.

Keywords: Dihydropyridine; Photochromism; Kinetics

1. Introduction

Photochemical activity of heterocyclic compounds of general formula shown in Fig. 1 has been investigated by several groups [1–19]. Typically, photoactive representatives of the family have their long-wavelength absorption edges in the near UV, irradiation into their UV absorption bands giving rise to a build-up of additional absorption bands in the visible; the resulting coloured species can then be bleached thermally. Molecular mechanisms of processes behind the photochromism of these compounds have been subject to some dispute – according to the Japanese group [1–6], the UV irradiation gives rise to an intramolecular aryl shift associated with the formation of a bicyclic compound which may then undergo irreversible reactions depending on the nature of the heterocyclic substituent X under ambient conditions. The Czech group [8–16] postulated that besides the aryl shift, following irreversible processes, a reversible 3,5-bridge formation may play a role in the photochromic activity of the compounds under study. More recently, Pirelahi et al. [17,18] put forward a modified scheme for thiopyrans ($X = S$) involving a hydrogen shift following the aryl shift.

A substantial part of the research mentioned above has been carried out on dihydropyridines ($X = N–R$) [2–4,7–9,12,13,15,19]. In particular, the kinetics of reactions involved in the colouration and bleaching of dihydropyridines has been reported in [8,12,13,19], most of the available experimental results being collected for 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (structure **I** in Fig. 2; hereafter referred to as DHP). The rate of the thermally bleaching process (determined in most cases from spectrophotometric measurements) was found to depend critically on conditions of the experiments: for example, the rate constant at ambient temperature determined for diluted solutions of DHP amount to ca. $5 \times 10^4\ s^{-1}$ [13], exceeding the corresponding value determined for polycrystalline samples by ca. 8 orders of magnitude [8,19]. The experiments performed on solutions of DHP [13] clearly indicate the first-order character of bleaching reactions, whereas the kinetics of the same processes occurring in polycrystalline samples was shown to be controlled by a distribution of the rate constants [8,19]. Moreover, results of preliminary non-isothermal measurements performed

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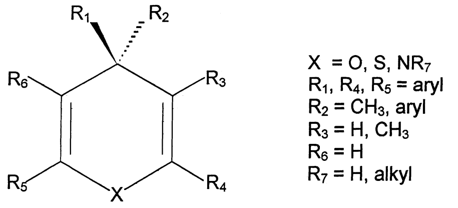

Fig. 1. Chemical formula of the family of photochromic compounds under study.

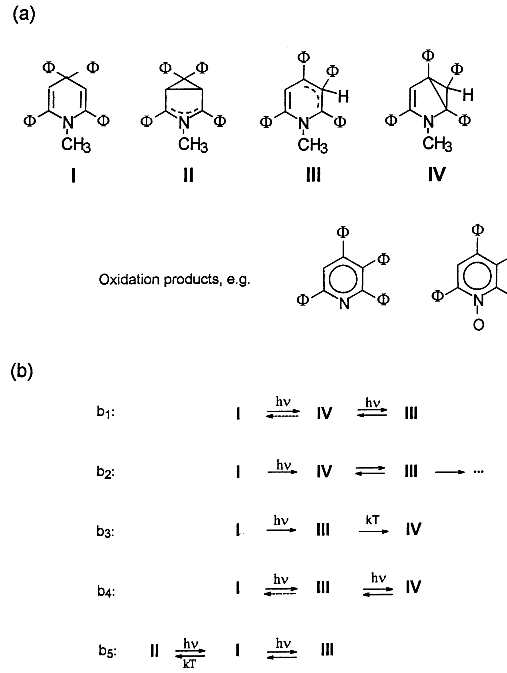

Fig. 2. (a) Chemical formula of the stable form of DHP (**I**), and of a few possible intermediate and final products of its photochemical reactions (adapted from [6,8,15,18]). Indicated are also possible oxidation products. (b) Simplified schemes of reactions put forward in the literature. (b1): [8]; (b2): [6]; (b3): [12]; (b4): [13]; (b5): [15]. The reaction scheme conforming to the results of this paper is shown in Fig. 9.

employing differential scanning calorimetry (DSC) [20] indicated that two bleaching processes possibly co-exist in DHP. Thus, it seemed worthwhile to undertake efforts aiming at clarifying details of the mechanism of the photochemical activity of DHP and related compounds.

We carried out measurements of the bleaching processes in DHP employing isothermal and non-isothermal techniques. Results of our experiments, supplemented with quantum chemical calculations, allow us to put forward a scheme of the colouration and bleaching processes in this material, well accounting for the existing experimental data.

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 [9]. Prior to measurements, polycrystalline samples of DHP were irradiated with a high-pressure Hg lamp supplied with a bandpass filter allowing us to shine into the UV absorption band of the material. The transmission range of the filter covered essentially the 313 nm emission of the lamp; however, the transmittance of the filter at shorter wavelengths (down to ca. 290 nm) was found small but non-negligible. The irradiation times ranged between ca. 10 s and 180 min, being typically much longer than the corresponding times employed in the experiments reported in [8].

The kinetics of bleaching reaction of oxygen-free DHP solutions was studied using a conventional flash-photolysis setup identical to that described elsewhere [13]. The samples were excited with a 15 ns pulse from a frequency-quadrupled NdYAG laser ($\lambda = 266$ nm); the bleaching kinetics was then measured by following the decay of the absorption band peaking at ca. 400 nm. Typically, the time span of the measurements reported here amounted to 5–10 ms, significantly exceeding that described in [13].

The spectra reported below were obtained from direct measurements of the absorption of polycrystalline DHP in KBr matrices. Crystallites of DHP were mixed with KBr (ca. 1 : 400), ground and pressed with $p = 2 \times 10^7$ Pa. The samples obtained in such a way were mounted in a temperature-controlled sample holder inside a Shimadzu UV-2101PC spectrophotometer, at ambient atmosphere. It should be noted that the absorption spectra obtained in such a way were found in agreement with those calculated from reflection spectra of DHP/MgO mixtures reported in earlier experiments [8,9].

The isothermal kinetics of the bleaching reaction in polycrystalline DHP was determined spectrophotometrically, by measuring the temporal evolution of the 550 nm band. The absorbances were calculated from reflection spectra of DHP/MgO mixtures using the Munk–Kubelka method. The measurements were carried out in the temperature range 290–350 K. Occasionally, the kinetic measurements were also performed on the DHP/KBr pellets; in this case, the absorbance of the samples was measured directly.

The non-isothermal kinetics was measured in most cases employing the DSC technique; occasionally, we also performed non-isothermal measurements on DHP/KBr pellets employing the spectrophotometric method. The calorimetric measurements were carried out with a Perkin Elmer DSC7 scanning calorimeter, within the temperature range 250–440 K. As was found in earlier experiments [8,20], thermally driven reverse reactions in polycrystalline DHP are quite slow at ambient temperature, thus allowing for a safe manipulation with the irradiated samples containing the coloured (meta-stable) product. Typically, masses of the samples used in the DSC experiments ranged between ca. 10 and 30 mg; due to a limited sensitivity of the method, the shortest irradiation time amounted to 15 min.

In all kinetic experiments reported in this paper, we studied the *thermal* bleaching. It should be pointed out, however, that we did not notice any appreciable changes in the kinetics of the reverse process(es) upon irradiating the samples containing the coloured species with the visible light absorbed by the coloured form of DHP.

3. Results

3.1. Spectra

Fig. 3 shows the absorption spectrum of the stable form of polycrystalline DHP measured at ambient atmosphere, and its evolution during a typical experimental cycle. The low-energy absorption band of DHP peaks around 300 nm, its long-wavelength edge extending to ca. 350 nm, in a good agreement with previously determined values [8]. Exposure of the samples to the UV irradiation results in the appearance of absorption bands centred at ca. 550 nm and 400 nm. It should be pointed out that the results reported in this paper, being generally in agreement with the results of earlier experiments [8], differ nevertheless in some details. In particular, our results seem to indicate that the reversibility of the colouration-thermal bleaching cycle is not complete: while the 550 nm peak can be completely bleached, the 400 nm one remains in the spectra even after a prolonged annealing, though its intensity varies to some degree (note that the experiments carried out in deaerated solutions [13] point out to a complete reversibility of the absorption at 400 nm). Moreover, the height of the former band could be restored nearly quantitatively during subsequent irradiation(s) only for short irradiation times (not exceeding ca. 5 min); longer irradiation times resulted in a decrease of the photochromic activity of the samples during successive cycles. We attribute these discrepancies to different experimental conditions, and in particular to a possible influence of ambient atmosphere on the formation of fatigue products in polycrystalline DHP.

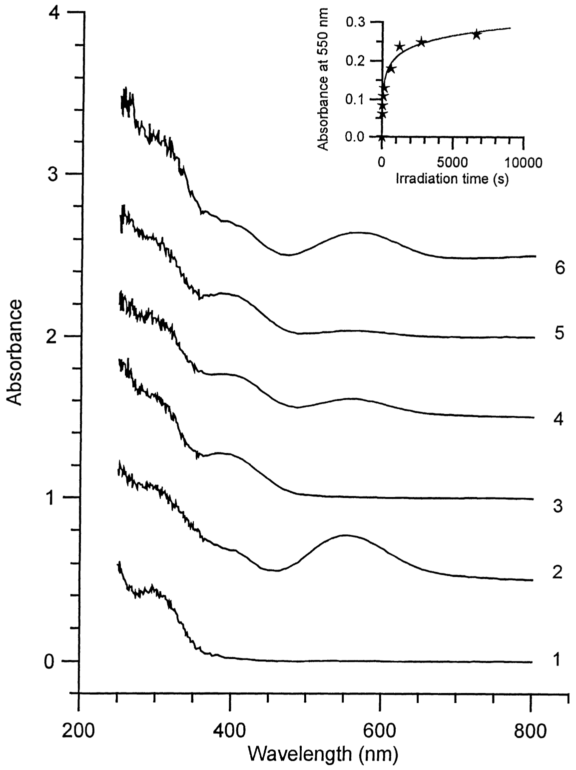

Fig. 3. Absorption spectra of polycrystalline DHP in a KBr matrix: (1) virgin sample; (2) after first irradiation with $\lambda = 313$ nm; (3) after annealing at 420 K; (4) after second irradiation; (5) after annealing; (6) after third irradiation. Curves (2)–(6) have been vertically displaced for the sake of clarity. Insert: dependence of the intensity of the 550 nm absorption band on the irradiation time. The line serves only to guide the eye.

3.2. Quantum-chemical calculations

As was mentioned above, the results published hitherto in the literature [2–4,8,9,12,13,15] do not provide an unambiguous picture of the mechanism of the photochromic activity of DHP and related compounds. An answer can be sought in quantum-chemical calculations, which should also explain the experimental results described in this paper.

The calculations reported in this paper were carried out in order to determine the geometry of the stable form of DHP (**I**), geometries of possible intermediate and final products of photochemical reactions (**II** to **V**; cf. Fig. 2), and of transition species between the products. Furthermore, calculations of the energies of the ground and low-lying excited states of the reactant, products and the transition states were performed. In such a way, the energetics of possible reaction paths has been determined.

The ground-state geometries of all structures shown in Fig. 2, and of all transition species were fully optimised using the semiempirical MNDO method of Dewar and Thiel [21]. In some cases we additionally employed the PM3 method [22]; the results obtained from both methods differed only in details as will be shown below. The excitation energies and reaction paths in the excited state were calculated using the semiempirical GRINDOL method [23], particularly suitable in this type of calculations. Two hundred singly excited configurations were included into the configuration interaction scheme.

The calculated energies of the ground states of the molecules **I**–**V** are listed in Table 1. It should be noted that the values obtained from calculations depend on the method employed; among other factors, the differences in energy are due to minor differences in the optimized geometries. The energies of the lowermost electronic transitions of the molecules **I**–**V** are given in Table 2. Again, some differences in the positions and intensities of the excitations should be noted, due to differences in the optimised geometries. Generally, however, our calculations reproduce the experimental results whenever a comparison is possible, being also

Table 1
Ground-state energies (relative to the energy of the stable form of DHP)[a]

Molecule[b]	Method of calculation		
	MNDO[c]	PM3[c]	PM3[d]
I	0	0	0
II	92	113	95
III	29	28	23
IV	17	55	85
V	−59	−18	

[a] All energies in kJ/mol.
[b] See Fig. 2.
[c] This work.
[d] [12].

in most points in a reasonable agreement with the results of earlier calculations of Böhm et al. [12].

The results given in Tables 1 and 2, together with calculated energies of the transition states allowed us to construct an energy diagram of possible reaction paths, schematically shown in Fig. 4.

3.3. Isothermal kinetics of bleaching

As was mentioned in an earlier paper [13], the photochromic activity of DHP in solutions could be detected only after a thorough elimination of traces of oxygen. The curve describing the decay of the absorption of deaerated DHP solutions in chloroform at ca. 400 nm, shown in Fig. 5, can be reasonably approximated by a superposition of two exponential decays, their time constants amounting to

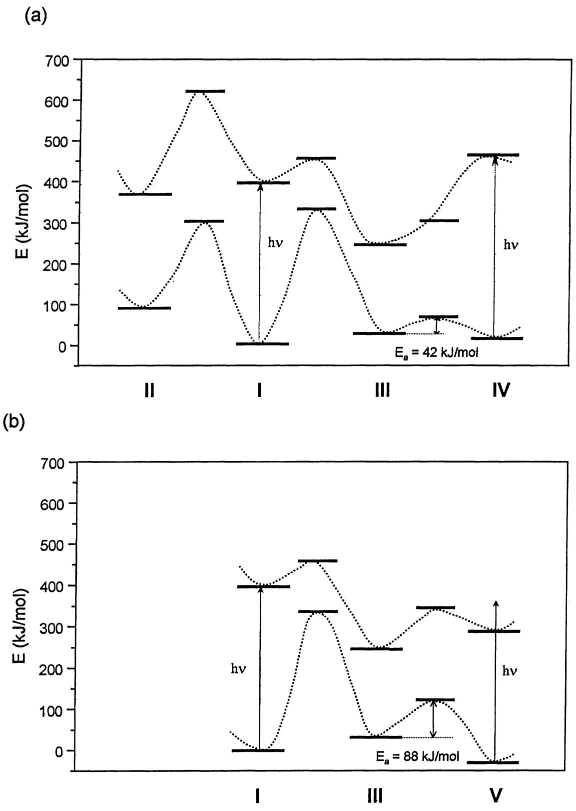

Fig. 4. Energies of the ground and first excited singlet states of the stable form of DHP, of possible products of photochemical reactions, and of transition species. The geometries were calculated using the MNDO method, and the energies with GRINDOL method. The numbering of the molecules corresponds to that in Fig. 2.

Table 2
Calculated low-energy electronic transitions in the stable form of DHP and in postulated products compared with the experimental spectra

Molecule	Calculated[a]		Calculated[b]		Calculated[c]		Experimental[d]	Experimental[e]
(cf. Fig. 2)	ν (cm^{-1})	f	ν (cm^{-1})	f	ν (cm^{-1})	f	ν (cm^{-1})	ν (cm^{-1})
I	33 550	0.0095	34 190	0.0021	34 830	0.0122	34 900	32 900
	39 480	0.5098	39 770	0.5721	38 240	0.2067	42 640	40 800
II	23 580	0.5678	21 500	0.7567	21 040	0.7912	25 000 (?)	24 700 (?)
III	18 040	0.3461	17 400	0.3561	17 540	0.3002	19 420	18 200
	28 600	0.3210	28 520	0.2805	25 770	00968	25 000 (?)	24 700 (?)
	30 120	0.0220	30 170	0.2275	26 340	0.0272	32 260	
	30 140	0.0275			27 580	0.0631		
	33 350	0.2853			27 690	0.0555		
					28 170	0.0677		
IV	37 380	0.3083	36 000	0.3891	36 600	0.0491		
					36 830	0.1946		
V	29 620	0.3887	29 880	0.4566				

Beyond the lowest-energy transitions, only the most prominent ones were shown.
[a] Geometry: MNDO; transitions: GRINDOL; this work.
[b] Geometry: PM3; transitions: GRINDOL; this work.
[c] Geometry: PM3; transitions: CNDO/S-CI [12].
[d] Chloroform solution [9,13].
[e] Polycrystalline sample [8] and this work.

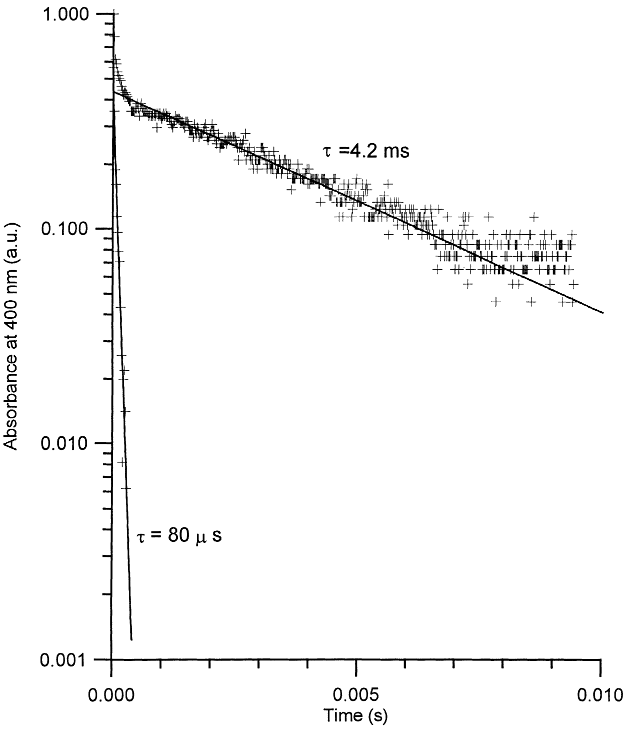

Fig. 5. Kinetics of bleaching of DHP in chloroform calculated from the decay of absorbance at 400 nm.

$(90 \pm 20)\mu$s and (4.2 ± 0.8)ms (average values taken from nine independent measurements). For short times, the value of the time constant is close to that given in [13], whereas the latter one has not been hitherto reported. Unfortunately, the equipment used did not allow us to measure the temperature dependence of the reaction kinetics, and thus we were unable to measure the activation energies of the processes.

The isothermal kinetics of the bleaching reaction in polycrystalline samples, monitored by following the temporal evolution of the 550 nm peak, is shown in Fig. 6. Although the measurements performed on solutions of DHP described above demonstrate that the processes involved are of the first order, the decays shown in Fig. 6(a) are clearly non-exponential, being instead reasonably fitted by the 'stretched-exponential' equation

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

with n standing for the concentration of the reactant (the coloured form of DHP), 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 [24,25], such a distribution may translate into a Gaussian distribution of activation energies.

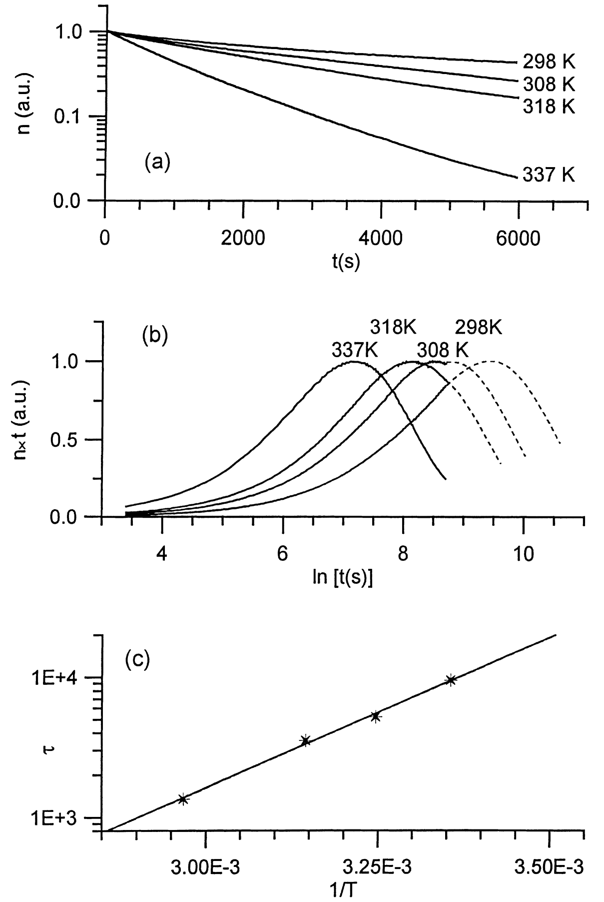

Fig. 6. Kinetics of bleaching of a polycrystalline DHP sample calculated from the decay of absorbance at 550 nm. The decay curves plotted in the conventional semilogarithmic coordinates (a), and in the $t \times n(t)$ vs. $\ln t$ coordinates (b). (c) The Arrhenius plot constructed from the results of (b).

In our previous paper [26], a straightforward method of analysis of non-exponential decays was put forward, allowing one to extract 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 replotted in the $[(Y \equiv t \times n(t))$ versus $\ln t]$ co-ordinates: the width of the resulting bell-shaped curves is related to the distribution width, and position of its maximum to the energy of the maximum of the distribution. We showed [26] that the full-width at half-maximum (FWHM) of the experimental curves (ω_{exp}, expressed in units of $\ln t$) is related to FWHM of the distribution of activation energies (Ω, assumed Gaussian and expressed in units of energy) via the equation

$$\omega_{\mathrm{exp}}^2 = \omega_0^2 + \left(\frac{\Omega}{RT}\right)^2, \tag{2}$$

where $\omega_0 \approx 2.45$ is the 'intrinsic' width of the Y curve. Moreover, for sufficiently narrow distributions, the maximum of the $Y(\ln t)$ are related to the energies of the distribution maxima via a simple relation

$$E_{\max} = RT\ln(A \times t_{\max}), \tag{3}$$

where A is the frequency factor.

The results of Fig. 6(a), re-plotted in the new co-ordinates and displayed in Fig. 6(b), can be well fitted with three temperature-independent parameters: $E_{\max} = 41.1$ kJ/mol,

$\Omega = 5.3$ kJ/mol, and $A = 2 \times 10^3\ \mathrm{s}^{-1}$. It is noteworthy that the ambient-temperature rate constant of the bleaching reaction, determined from our measurements, is of the order of $10^{-4}\ \mathrm{s}^{-1}$, i.e. is several orders of magnitude lower than any of the rate constants measured in solution.

3.4. Non-isothermal kinetics of bleaching

A complete determination of kinetics parameters from isothermal measurements may often be time-consuming; moreover, performing a series of reproducible measurements may become a problem in some samples, due to the influence of unwanted side processes (as is the case with DHP). Difficulties of this type can be overcome by using thermally stimulated (non-isothermal) techniques. The method essentially consists in measuring a kinetic response of a sample upon linearly increasing its temperature. A good example of the method is the DSC technique, which was employed to study the reaction in polycrystalline DHP [20,27]. 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 (cf. Fig. 7(a)). The difference between the first and subsequent runs, hereafter referred to as the excess heat flow (Φ_r) should provide information about the enthalpy of bleaching processes. Integration of the experimental $\Phi_r(T)$ curves yielded the values ranging between −2.5 and −5 kJ/mol (calculated for the total amount of DHP in the samples). Unfortunately, we were unable to determine the degree of conversion of DHP into the coloured product, thus no quantitative determination of ΔH_r was possible.

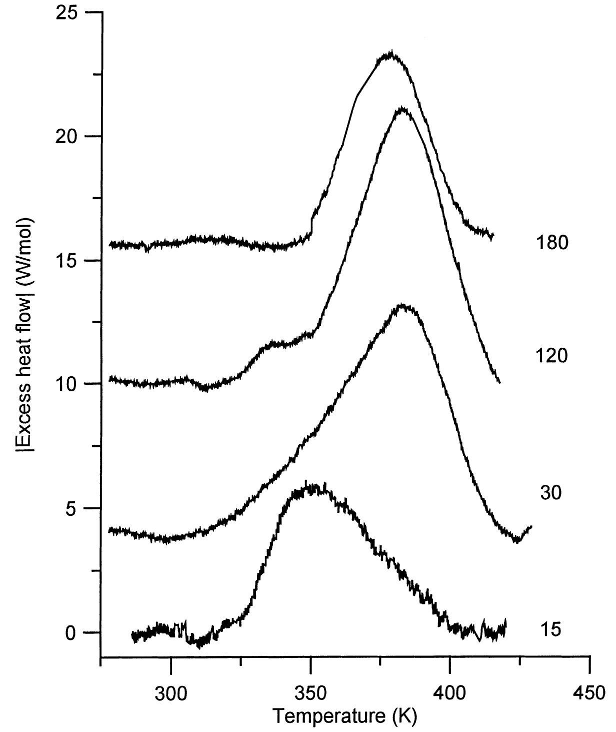

Fig. 7. Dependence of the shape of the excess heat flow peak on the irradiation time. The parameter is the irradiation time (in minutes).

We performed measurements attempting to determine the magnitude of the DSC response on the irradiation time. The results are shown in Fig. 7(b): the main feature of heat flow curves measured on samples irradiated for a short time (15 min) was a peak at ca. 350 K, with a shoulder at higher temperatures. Further irradiation resulted in the build up of a peak at ca. 380 K; the 350 K peak, first discernible as a shoulder, practically disappears in the heat flow curves measured on samples irradiated over ca. 180 min. The result seems to point out to a co-existence of two bleaching processes.

Bearing in mind the results of the isothermal measurements reported above, which indicated the presence of a distribution of rate constants, we employed the fractional heating DSC method [27], allowing in principle to separate possible independent processes and to gather information about a distribution of activation energies. The latter technique consists of a sequence of heating runs to successively increasing temperatures (cf. Fig. 8 (a)); the slopes of the

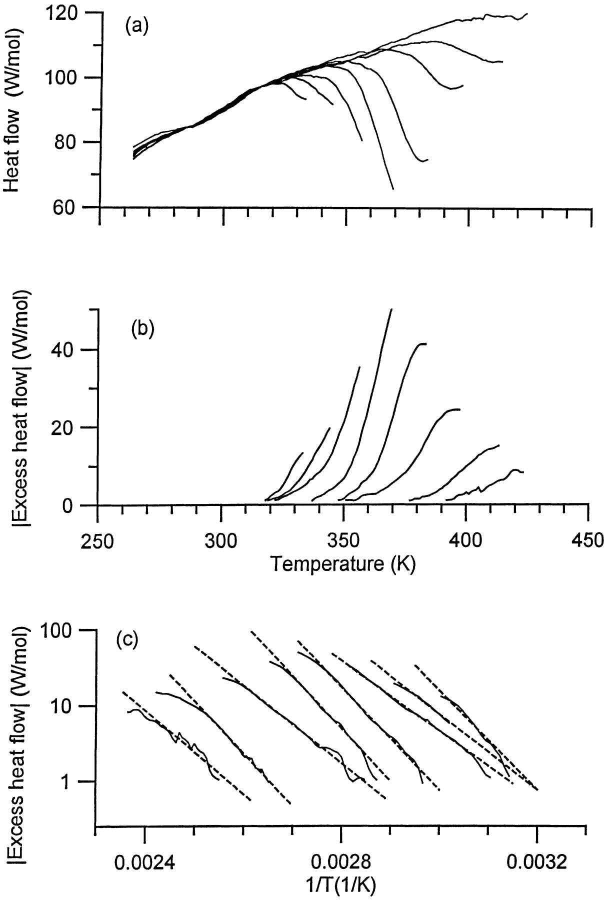

Fig. 8. Fractional heating DSC experiment. A series of the heating runs measured after irradiation of the sample at 290 K (a), and excess heat flow curves obtained from (a) after subtraction of baselines, plotted in linear (b), and Arrhenius (c) coordinates.

measured responses carry information about the activation energies and their distribution. Typical experimental results are shown in Fig. 8. We found that the activation energies determined from the Arrhenius fits to the experimental curves are burdened with a substantial spread, resulting mainly from problems with a reliable determination of baselines. Thus the temperature dependence of the activation energy could not be reliably determined: the average value obtained from measurements performed on 10 samples was found to amount to (130 ± 30)kJ/mol, depending on the sample crystallinity, conditions of irradiation etc. It should nevertheless be noted that the obtained value, in spite of the considerable spread, 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: preliminary results of our non-isothermal measurements of the kinetics of bleaching of the 550 nm band in polycrystalline DHP [28] yield the activation energy equal to ca. 60 kJ/mol. Thus we have been lead to believe that in fact we observed signatures of two independent bleaching processes.

4. Discussion

The experimental results presented in this paper point out to the co-existence of two independent bleaching processes, thus suggesting that there might exist two parallel paths accounting for the photochromic activity of DHP. It would be tempting to link these two processes with the two mechanisms postulated in the earlier papers [8–16], i.e., the intramolecular phenyl shift and the 3,5-ring closing. However, the quantum chemical calculations, whose results are described in the preceding section, clearly indicate that the latter reaction, i.e. a reversible 3,5-ring closing (**I** ⇔ **II**, cf. Fig. 2) can be ruled out in spite of a reasonable agreement between the calculated energy of the lowest electronic transition in **II** and the 400 nm band appearing in our samples upon irradiation. Our results show that the barriers for such a reaction are far too high, both in the ground and in the excited state. The most plausible reaction scheme, based on the results of our calculations as well as on the analysis of the mechanisms put forward in the literature, and well accounting for our experimental results, can be presented in the following way.

Irradiation of the stable form of DHP (**I**) results in formation of the coloured from **III** via an intramolecular phenyl shift. According to the calculations, the primary photochemical process should be essentially irreversible. The bleaching process would then be associated with a 2,4-bridge formation (**III** → **IV**) [1–6] and/or an intramolecular hydrogen shift (**III** → **V**) [17,18]. Note that for both processes the barriers in the excited state are higher than those in the ground state, thus these processes should essentially be only thermally driven as was indeed found in our experiments. The closing processes in the photochromic cycle would correspond to the **IV** → **III** and/or **V** → **III** reactions, both photochemically driven. In other words, absorption of the 313 nm light should result in excitation of **I**, but also of **IV** and **V**, present in the samples after the first irradiation.

The reaction scheme, presented in Fig. 9, seems to reconcile the results obtained from various experimental techniques and from quantum-chemical calculations. In particular, the calculations point out to a possible co-existence of two parallel bleaching processes: a 2,4-bridge formation, associated with the energy barrier equal to ca. 42 kJ/mol, and an intramolecular hydrogen shift, controlled by the barrier amounting to ca. 88 kJ/mol. Both of the latter reactions should be reversible: the coloured form should be reproduced via photochemically driven processes. In accordance with these predictions, our experiments indeed point out to the existence of two bleaching processes, controlled by the energy barriers amounting to ca. 40–50 kJ/mol and 100–150 kJ/mol. While the agreement between the lower energies appears quite good, the calculated and experimental energies of the latter process differ by ca. 60%. It should be

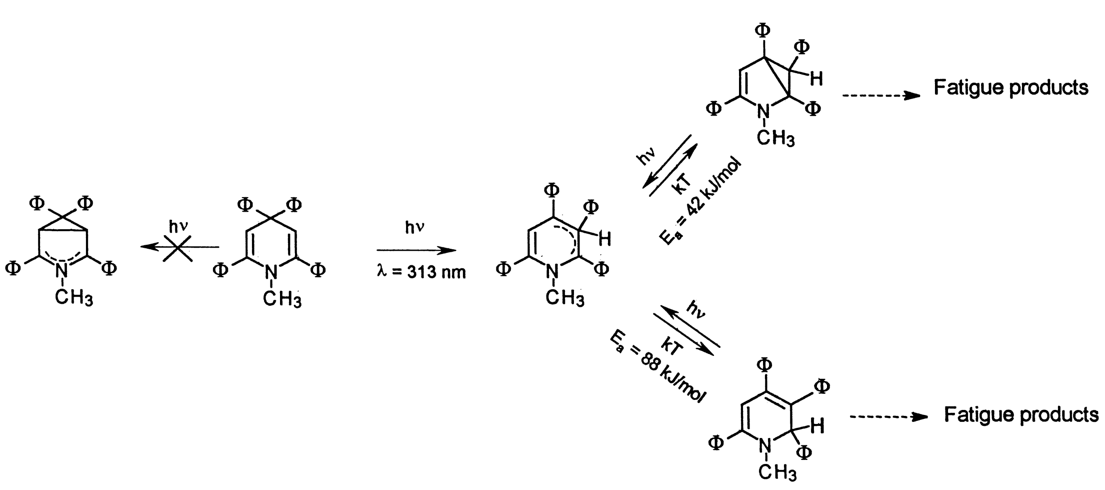

Fig. 9. Postulated reaction scheme (see text for further discussion).

pointed out, however, that our calculations have been carried out for isolated molecules whereas the experiments have been performed on polycrystalline samples, in which the kinetics is likely to be influenced by interactions with the environment, minor changes in geometries, presence of defects etc. Moreover, one must not forget about the uncertainty in values of the activation energies determined from our measurements due to purely experimental factors.

A similar argument can also be used to answer another question arising on a closer examination of the diagram shown in Fig. 9. According to the diagram, the 313 nm light quanta should not be able to excite molecules **IV**, thus, in principle, they cannot drive the **IV** → **III** reaction. We believe, however, that the dependence of the calculated excitation energies on the molecular geometry discussed in the preceding section, as well as possible dependences of these energies on interactions of the excited molecules with environment, may result in a lowering of the energy of the S_1 state of the molecules **IV** in crystals. One should also bear in mind a contribution from short-wavelength light present in the spectrum of the source of light used in our experiments (cf. Section 2 of this paper).

The reaction kinetics (and hence the scheme of Fig. 9) may be additionally complicated by presence of metastable species such as long-lived radicals. It should be realised that presence of such species is not inconceivable in irradiated crystalline DHP as at least two steps (**I** → **III** and **III** → **V**) are likely to involve radical formation.

Our experiments also show, in accordance with earlier reports [2,4,6], that the reversibility of the system is rather poor. Thus irreversible fatigue reaction(s) should also be taken into account, the most probable process being oxidation potentially yielding several products such as a pyridine derivative, its oxide, etc (cf. Fig. 2). One might speculate that the presence of the latter products accounts for the non-erasable contribution to the 400 nm peak in the spectra. At present, however, we cannot offer any direct evidence supporting this hypothesis.

5. Conclusions

We studied the energetics and kinetics of the bleaching process in DHP. The experimental results: spectra of polycrystalline DHP and their evolution during successive irradiation-bleaching cycles, and calorimetric measurements, compared with results of quantum-chemical calculations, allowed us to put forward a mechanism of the photochromic activity of the material under study. According to our model, the primary photochemical process – intramolecular phenyl shift – is essentially irreversible; the photochromic cycle consists of two reversible parallel reactions: a 2,4-ring closing and a hydrogen shift.

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