ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 129 (1999) 81–87

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

On the mechanism of bleaching reactions in a photochromic dihydropyridine derivative

Juliusz Sworakowski [a,*], Stanislav Nešpůrek [b], Józef Lipiński [a], Aleksandra Lewanowicz [a]

[a] *Institute of Physical and Theoretical Chemistry, Politechnika Wrocławska, 50-350 Wrocław, Poland*

[b] *Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague, Czech Republic*

Received 21 June 1999; accepted 13 August 1999

Abstract

Kinetics of thermally driven reactions in solutions of photochromic 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 species absorbing at ca. 520 nm, produced upon UV irradiation of solutions of DHP in chloroform and in chloroform/PMMA. The decay curves can be interpreted assuming a contribution from two coloured species produced in a sequence of elementary processes. A comparison of quantum-chemical calculations with results of spectroscopic and kinetic measurements seems to indicate that the initial step following an electronic excitation of DHP involves radical formation, the absorption around 520 nm being probably associated with $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_2$ transitions in one of intermediate products.
©1999 Elsevier Science S.A. All rights reserved.

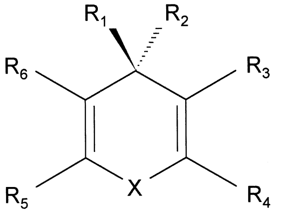
Keywords: Dihydropyridine; Photochromism; Kinetics

---

1. Introduction

Photochemical properties of derivatives of dihydropyridines, pyranes, and thio- and selenopyranes — a family of photochromic compounds of the general formula shown in Fig. 1 — have been studied for some time [1–19] but details of the reactions responsible for their photochromic behaviour have been subject to some dispute: an intramolecular aryl shift associated with the formation of a bicyclic compound [1–6], a reversible 3,5-bridge formation [8–16] and a hydrogen shift following the aryl shift [17,18] have been put forward.

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], 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 absorption spectra of the stable and coloured forms of solutions and polycrystalline samples of DHP are similar (cf. Fig. 3), the similarity indicating that the same species are involved in the photochemical processes in both cases. The stable form of DHP has its long-wavelength absorption edges in the near UV, irradiation into its UV absorption band giving rise to a build-up of additional absorption bands which in solutions are located at ca. 520 nm (shifting to ca. 550 nm in solid samples), and around 400 nm. The resulting coloured species can be bleached thermally, the rate of the latter process depending critically on conditions of the experiments [8,13,19]. The experiments performed in the microsecond range on solutions of DHP [13] were interpreted assuming a first-order character of bleaching reactions, whereas the kinetics of much slower bleaching processes occurring in polycrystalline samples was interpreted assuming additionally a distribution of the rate constants [8,19].



X = O, S, NR_7
R_1, R_4, R_5 = aryl
R_2 = CH_3, aryl
R_3 = H, CH3
R_6 = H
R_7 = H, alkyl

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

In our previous paper [19], we put forward a reaction scheme according to which the primary photochemical

---

[*] Corresponding author. Tel.: +48-71-3203468; fax: +48-71-3203364
E-mail address: sworakowski@kchf.ch.pwr.wroc.pl (J. Sworakowski)

1010-6030/99/$ – see front matter ©1999 Elsevier Science S.A. All rights reserved.
PII: S1010-6030(99)00171-9

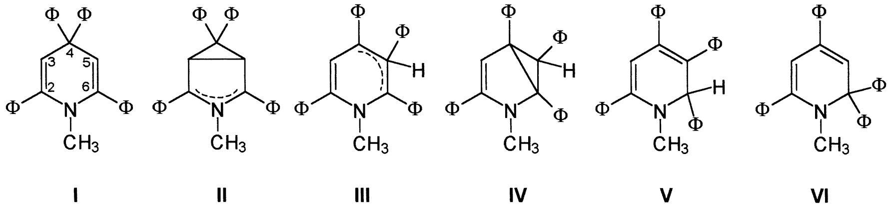


Fig. 2. Chemical formula of the stable form of DHP (I), and of possible intermediate and final products of its photochemical reactions. The numbering of the molecules corresponds to that employed in our previous paper [19].

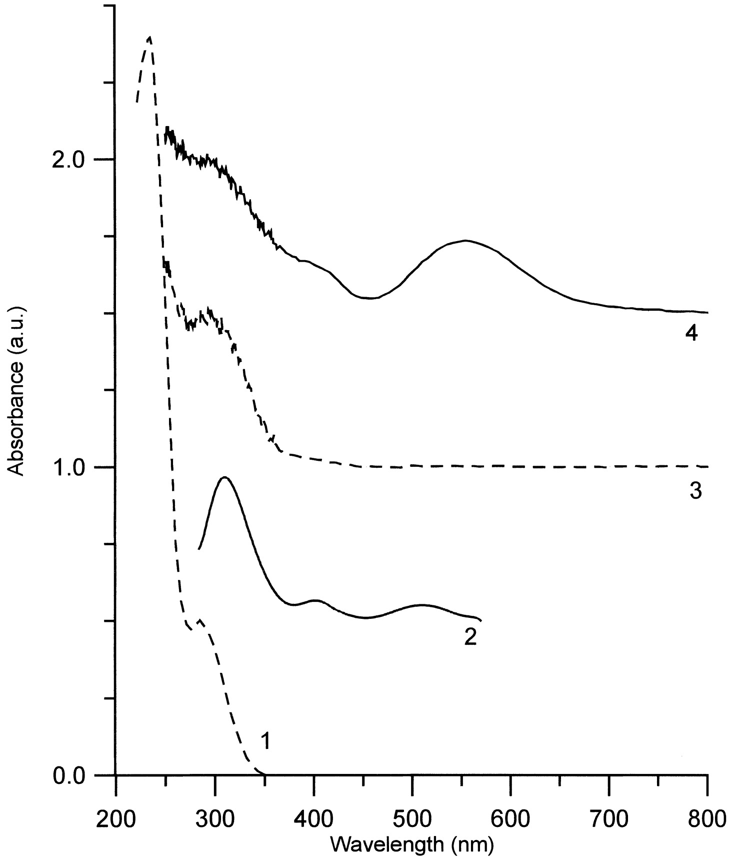


Fig. 3. UV-Vis spectra of solutions and polycrystalline DHP. Broken lines: DHP prior to irradiation; full lines: after irradiation with UV light. Curves 1 and 2: acetonitrile solution (adapted from [13]); curves 3 and 4: polycrystalline DHP in KBr matrix (adapted from [19]). To facilitate comparison, the curves 2–4 have been vertically displaced by 0.5, 1 and 1.5 a.u., respectively.

process — intramolecular phenyl shift — is essentially irreversible; the photochromic cycle consists of two possible parallel reactions: a 2,4-ring closing and a hydrogen shift. Our results indicated that the 3,5-bridge formation is impossible in DHP due to high energy barriers in both ground and excited states. The model, apparently reconciling most of the existing experimental material (in particular, spectra and kinetic measurements) with results of quantum-chemical calculations, leaves nevertheless a few questions which should be addressed.

Previously reported ambient-temperature kinetic experiments performed on solutions of DHP, showed that the bleaching in the microsecond range, if interpreted as a first-order process, is characterised by the rate constant amounting to ca. $5 \times 10^4\,\mathrm{s}^{-1}$ [13], whereas preliminary results of similar measurements in the millisecond range [19] point to the presence of another slower process with the rate constant of the order of 10^2–$10^3\,\mathrm{s}^{-1}$. It should be noted that the kinetics reported in [13] and in [19] were measured in different conditions: the former one [13] was monitored by following decays of the absorption at ca. 390 nm, whereas the latter paper [19] contained results of measurements at 520 nm. Furthermore, a closer inspection of the decays published in [19] reveals the presence of a plateau around 1 ms (see the curves shown in Section 3.2 of this paper), which cannot be accounted for by assuming two parallel processes as was done in [19]. Thus, the question arises concerning the nature of the absorbing species and sequence of elementary processes.

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]. The bleaching experiments reported in this paper were carried out using chloroform solutions of DHP, the solute concentrations ranging between 1×10^{-4} and 4×10^{-4} mol dm^{-3}. We also performed measurements of the decay kinetics in function of the solution viscosity. In this case, we used chloroform solutions of DHP additionally containing PMMA ($M_{\mathrm{av}}\approx5\times10^{5}$ g mol^{-1}) at concentrations reaching 0.11 g cm^{-3}. The viscosities of the solutions obtained in such a way reached ca. 4×10^{-2} Nm^{-2} s.

The kinetics of the 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 Nd : YAG laser ($\lambda=266$ nm); the bleaching kinetics was then measured by following the decay of the absorption band peaking at ca. 520 nm. Typically, the time span of the measurements reported in this paper amounted to 5–10 ms.

We also carried out auxiliary measurements on solid samples of DHP in KBr matrices. In this case, crystallites of DHP were mixed with KBr (ca. 1 : 400), ground and pressed at $p=2\times10^{7}$ 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. The samples 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.

3. Results

3.1. *Quantum-chemical calculations*

It was mentioned above (see also Fig. 3) that the irradiation of DHP results, among others, in the appearance of a band peaking at ca. 400 nm. On the other hand, the results of quantum-chemical calculations reported in [19], indicate that none of the molecules displayed in Fig. 2 should exhibit any appreciable absorbance at 400 nm. However, since the reaction resulting in the production of coloured species involves rearrangements of chemical bonds, it is likely that radicals are produced. Indeed, the quantum-chemical calculations described in this section, as well as preliminary results of solid-state ESR experiments, seem to confirm such a possibility. It should, however, be noted that the radicals need not be identified with transition species for intramolecular reactions in which rearrangements of molecules occur without a complete breaking of bonds between moieties involved.

The calculations reported in this section supplement those published in [19]: in addition to the geometries of the stable form of DHP, possible intermediate and final products of photochemical reactions (cf. Fig. 2), as well as of transition species between the products, we carried out calculations of the geometries of radicals whose formation seemed probable: (i) a radical formed from the stable form of DHP (molecule I) by breaking the C(4)–phenyl bond (hereafter referred to as RA), and (ii) a radical formed from III by breaking the C(3)–H bond (RB). Moreover, calculations were performed of the energies of the ground and low-lying excited states of all species involved in the postulated reaction scheme.

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], whereas the semiempirical GRINDOL method [22] was employed to calculate the excitation energies. Two hundred singly excited configurations were included into the configuration interaction scheme. The calculated energies of the ground states and of the excited states of all relevant species are listed in Table 1. For most species, we display only the energies of the lowest singlet and triplet states,

Table 1
Energies of the ground states, and the lowest excited singlet states in DHP (I), and possible transition and metastable species produced in a sequence of photochemical reactions. The symbols denoting the molecules are identical as in Fig. 2. All values are given in kJ mol^{-1}, relative to the energy of the ground state of the stable form of DHP

Molecule	Ground and lowest excited states of molecules				Ground and lowest excited states of radicals	
	S0	T1	S1	T2	Ground state	Excited states
Stable and metastable molecules (see Fig. 2)						
I	0	290	402			
III	29	48	247	296		
IV	17	306	465	378		
V	−59	167	293	295		
VI	19		377			
Transition species for purely intramolecular reactions						
(I–III)	335	318	457	550		
(III–IV)	71	113	305	338		
(III–V)	117	147	344	393		
(III–VI)	298		401			
Radicals						
RA[a]					177	309
						456
Rb[b]					195	356
						477

[a] RA + phenyl; RA ≡ I with phenyl detached from the position 4.
[b] RB + H; RB ≡ III with hydrogen detached from the position 3.

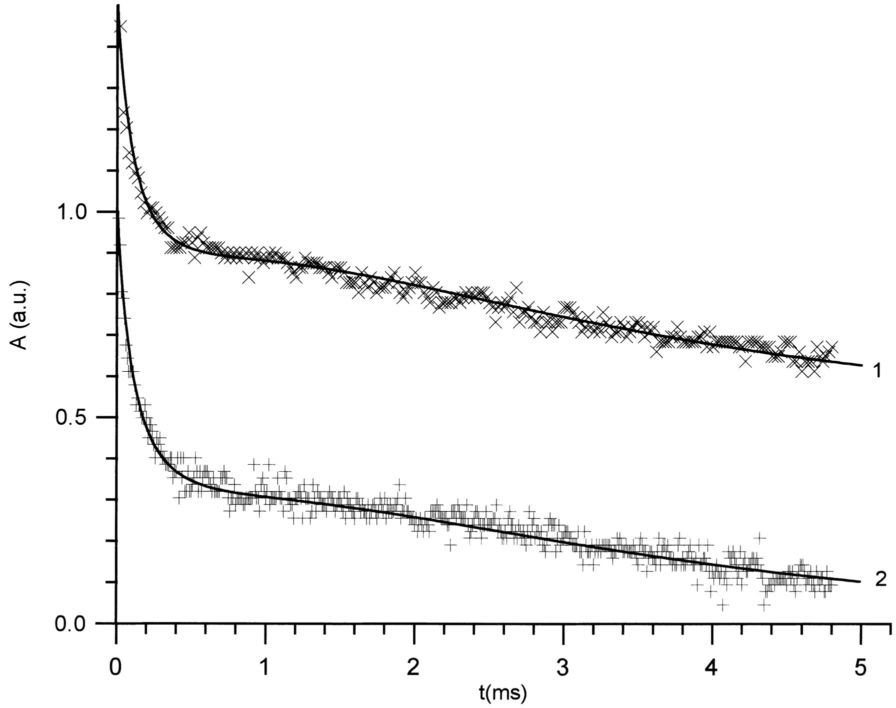


Fig. 4. Ambient-temperature bleaching kinetics of DHP in solution. (1) Pure chloroform (relative viscosity equal to 0), (2) chloroform + PMMA (relative viscosity equal to 86). Full lines are the reconstructed curves calculated using Eq. (10) and the rate constants determined from the fits. The curve 1 has been vertically shifted by 0.5 a.u.

whereas for the radicals the energies of two lowest-lying states are given: our calculations show that in some radicals taken into consideration there exist excited states at ca. 11,000–12,000 cm^{-1}, possibly deciding about the reaction path, as well as states at ca. 25,000 cm^{-1} which might be responsible for the absorption at 400 nm. A more detailed discussion of the results will be given in Section 4, at this point we only want to turn the reader's attention to the fact that the calculated energy of the lowest excited state of the RA radical is located well below that of the transition state whose position would determine the barrier for a purely intramolecular phenyl shift.

3.2. Kinetic equations and analysis of experimental decays

As was mentioned above, the experiments were performed in chloroform solutions, in some cases containing additionally PMMA which changed the solution viscosity being otherwise neutral. Fig. 4 shows experimental decays of the absorbance at 520 nm, measured at ambient temperature for two limiting cases: a chloroform/DHP solution (viscosity equal to ca. $0.5\times10^{-3}\,\mathrm{Nm^{-2}\,s}$), and for a chloroform/PMMA/DHP solution (ca. $40\times10^{-3}\,\mathrm{Nm^{-2}\,s}$). Irrespective of the viscosity, all curves were found to consist of an initial section of a rapid decay, separated from a slower decay by a clearly discernible plateau around 0.8–1.5 ms. This type of decay can be fitted with the following equation

$$A(t)=\xi_1\exp(-k_{\mathrm{short}}t)+\xi_2\exp(-k_{\mathrm{long}}t)-\xi_3\exp\left(-k_{\gamma}t\right), \tag{1}$$

where A is the absorbance normalised to its initial value, and ξ_1, ξ_2 and ξ_3 stand for time-independent positive coefficients. In our previous paper [19], we attributed the two decays to two parallel processes; such a scheme, however, cannot account for the presence of the plateau: in the simplest case, such a shape of the bleaching kinetics should involve a sequence of consecutive reactions, with two species absorbing at 520 nm. It should also be stressed at this point that the type of kinetics described by Eq. (1) requires that the absorbing molecules be disconnected, i.e., separated by at least one non-absorbing species in the sequence of elementary processes.

Taking into account results of the quantum-chemical calculations presented in Section 3.1 (see also the discussion in Section 4), we put forward a simplified sequence of elementary reactions as shown in Fig. 5. The symbols denoting molecules are those used in Fig. 2, RA is the radical absorbing at 400 nm, and X is an unknown intermediate product whose nature at this stage of research can only be subject to speculations. The model presented in this paper modifies initial stages of photochemical processes following the excitation of DHP, put forward in [19]. First, breaking one of the C(4)–phenyl bonds and formation of the radicals (RA and Φ) opens possible paths for the recombination, resulting in the reproduction of stable DHP (molecule I), and/or in

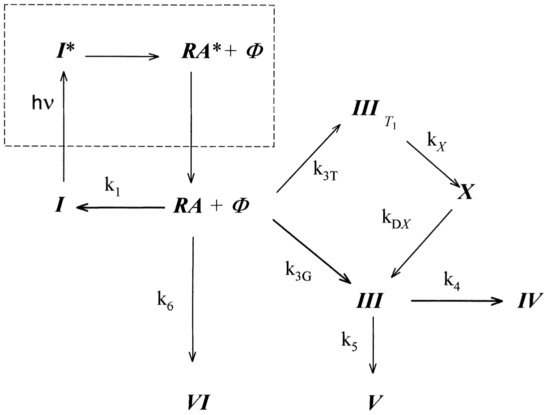


Fig. 5. The proposed sequence of elementary processes in DHP following a UV pulse. The processes inside the dashed line box occur at times shorter than the time scale of the experiment described in this paper.

formation of the coloured species (molecule III), and, possibly, also of a molecule VI. Note that the latter molecule has a relatively low-lying ground state and may appear quite stable. Moreover, its optical gap almost coincides with that of the molecule V (29,900 cm^{-1}versus 29,400 cm^{-1}, cf. Table 1). Secondly, the recombination of radicals may result in formation of the molecules I, III and VI in both, S_0 and T_1 states. For the purpose of this paper, of interest is a possibility of the formation of the S_0 and T_1 states of the molecule III. Our calculations indicate that the optical gaps for the $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_2$ absorption are quite close (18,000 cm^{-1}versus 20,700 cm^{-1} cf. Table 1); use of other methods of calculations (not reported here) results in an even better agreement [23].

The above scheme can be solved for the concentrations of the relevant products (the RA radical, and the ground-and triplet state forms of III).

$$\frac{\mathrm{d}c_{\mathrm{RA}}}{\mathrm{d}t} = -kc_{\mathrm{RA}}c_{\Phi}, \tag{2}$$

$$\frac{\mathrm{d}c_{\mathrm{T}}}{\mathrm{d}t} = k_{3\mathrm{T}}c_{\mathrm{RA}}c_{\Phi} - k_{\mathrm{X}}c_{\mathrm{T}}, \tag{3}$$

$$\frac{\mathrm{d}c_{\mathrm{G}}}{\mathrm{d}t} = k_{3\mathrm{G}}c_{\mathrm{RA}}c_{\Phi} + k_{\mathrm{DX}}c_{\mathrm{T}} - k_{\mathrm{DG}}c_{\mathrm{G}}, \tag{4}$$

where

$$k = k_1 + k_3 + k_6, \tag{5}$$

$$k_3 = k_{3\mathrm{T}} + k_{3\mathrm{G}}, \tag{6}$$

$$k_{\mathrm{DG}} = k_4 + k_5. \tag{7}$$

Let us note that bleaching of the RA radical is a bimolecular process. In case of its geminate recombination with phenyl this results in a second order kinetic equation; consequently the solutions for temporal dependence of the concentration of RA and Φ should read

$$c_{\mathrm{RA}} = c_{\Phi} = a\left(1 + \frac{t}{\tau}\right)^{-1}, \tag{8}$$

where a is the initial concentration of RA produced by a light flash, and $\tau = 1/ka$.

If the recombination of the RA radical is a second-order process, then a general solution of Eqs. (3) and (4) in closed forms is impossible; let us note, however, that reasonably accurate solutions can be obtained if $k_3 \gg k_{\mathrm{DT}}$, $k_3 \gg k_{\mathrm{DX}}$, which seems to be the case in the experiments described in this paper. Then, irrespective of the type of the recombination kinetics, initial concentrations of the molecules III in the T_1 and S_0 states amount to

$$c_{\mathrm{T}}(t \approx 0) = \eta_{\mathrm{T}}a \tag{9}$$

$$c_{\mathrm{G}}(t \approx 0) = \eta_{\mathrm{G}}a \tag{10}$$

where $\eta_i = k_i/k$. Hence the expressions for $c_{\mathrm{T}}(t)$ and $c_{\mathrm{G}}(t)$ read

$$c_{\mathrm{T}} = \eta_{\mathrm{T}}a\exp(-k_{\mathrm{X}}t), \tag{11}$$

$$\begin{aligned} c_{\mathrm{G}} = {} & \eta_{\mathrm{G}}a\exp(-k_{\mathrm{DG}}t) + \eta_{\mathrm{T}}a\left[\kappa_1\exp(-k_{\mathrm{DG}}t)\right. \\ & \left. -\kappa_2\exp(-k_{\mathrm{DX}}t) + \kappa_3\exp(-k_{\mathrm{X}}t)\right], \end{aligned} \tag{12}$$

where κ_i ($i = 1, 2, 3$) are combinations of the rate constants

$$\kappa_1 = \frac{k_{\mathrm{X}}k_{\mathrm{DX}}}{(k_{\mathrm{DG}} - k_{\mathrm{X}})(k_{\mathrm{DG}} - k_{\mathrm{DX}})}, \tag{13}$$

$$\kappa_2 = \frac{k_{\mathrm{X}}k_{\mathrm{DX}}}{(k_{\mathrm{DG}} - k_{\mathrm{DX}})(k_{\mathrm{DX}} - k_{\mathrm{X}})}, \tag{14}$$

$$\kappa_3 = \frac{k_{\mathrm{X}}k_{\mathrm{DX}}}{(k_{\mathrm{DG}} - k_{\mathrm{X}})(k_{\mathrm{DX}} - k_{\mathrm{X}})}. \tag{15}$$

Introducing the Lambert-Beer law, one finally obtains an expression describing the temporal evolution of the absorbance at 520 nm, equivalent to Eq. (1)

$$A = \alpha\exp(-k_{\mathrm{X}}t) + \beta\exp(-k_{\mathrm{DG}}t) - \gamma\exp(-k_{\mathrm{DX}}t), \tag{16}$$

where A stands for the absorbance normalised to its initial value, and α, β and γ are time-independent parameters defined by the equation

$$\alpha = \frac{\varepsilon_{\mathrm{T}}\eta_{\mathrm{T}} + \varepsilon_{\mathrm{G}}\eta_{\mathrm{T}}\kappa_3}{\varepsilon_{\mathrm{T}}\eta_{\mathrm{T}} + \varepsilon_{\mathrm{G}}\eta_{\mathrm{G}}}, \tag{17}$$

$$\beta = \frac{\varepsilon_{\mathrm{G}}\eta_{\mathrm{G}} + \varepsilon_{\mathrm{G}}\eta_{\mathrm{T}}\kappa_1}{\varepsilon_{\mathrm{T}}\eta_{\mathrm{T}} + \varepsilon_{\mathrm{G}}\eta_{\mathrm{G}}}, \tag{18}$$

$$\gamma = \frac{\varepsilon_{\mathrm{G}}\eta_{\mathrm{T}}\kappa_2}{\varepsilon_{\mathrm{T}}\eta_{\mathrm{T}} + \varepsilon_{\mathrm{G}}\eta_{\mathrm{G}}}, \tag{19}$$

with ε_i being molar absorbances of species absorbing at 520 nm. The rate constants of the processes controlling the temporal evolution of the absorbance can be determined in the following way: exponential fits to the short-and long-time sections of experimental curves allow one to estimate two rate constants: k_{short} and k_{long}, and to calculate the function $A_{\mathrm{short}}(t) \equiv \xi_1 \exp(-k_{\mathrm{short}}t)$. The rate constants determined in such a way should be close to k_{X} and k_{DG}.

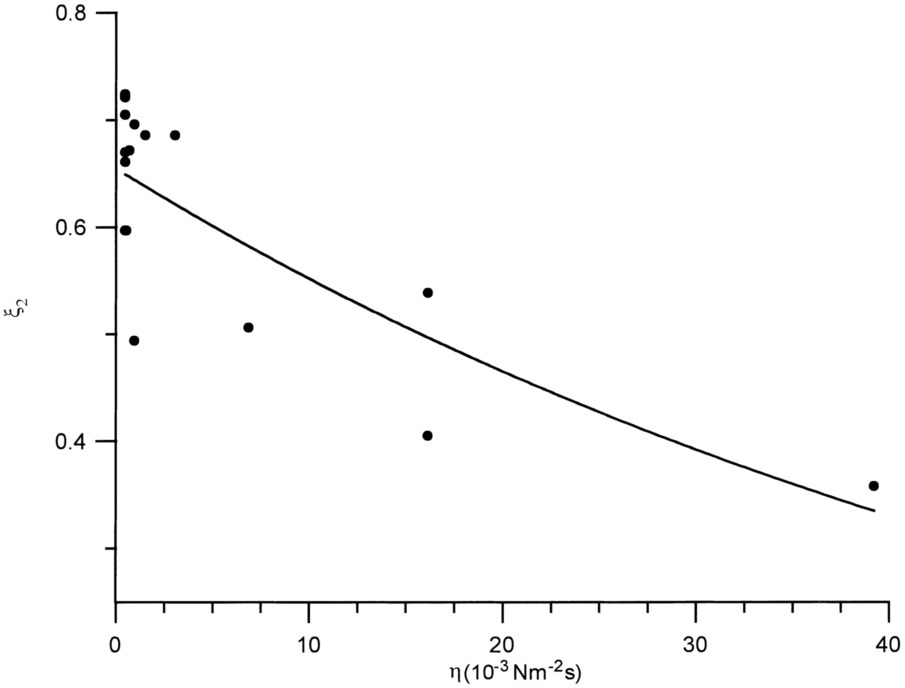


Fig. 6. Viscosity dependence of the parameter ξ_2 (cf. Eq. (1)). The line serves only to guide the eye.

Unfortunately, the functional form of Eq. (15), symmetrical with respect to the above rate constants, does not allow one to decide whether $k_X > k_{DG}$ (i.e., $k_{short} = k_X$) or $k_X < k_{DG}$ (i.e., $k_{short} = k_{DG}$). The third time constant (k_{DX}) can be determined from the condition for a maximum of the temporal dependence of the $[A(t) - A_{short}(t)]$ function. The values of the rate constants obtained in such a way are then optimised to achieve the best fit to experimental points.

Using the above equations, we analysed the experimental curves measured on the DHP solutions in pure chloroform, and in chloroform/PMMA of various viscosities. Three time constants were determined in the way shown above, the accuracy of the determination being checked in all cases by fitting the entire curve with Eq. (16). The average values determined from 6 independent measurements performed on pure chloroform solutions of DHP were found to amount to $(6000 \pm 1000)\,s^{-1}$; $(500 \pm 100)\,s^{-1}$ and $(1200 \pm 300)\,s^{-1}$. To within the accuracy of our measurements, the viscosity of the medium seems to influence to some extent the kinetics of the processes under study: we observed a systematic trend in the viscosity dependence of the parameter ξ_2 (cf. Fig. 6) as well as, possibly, the rate constant k_{DG}. The spread of experimental results, however, does not allow us to draw any further-reaching conclusions.

4. Discussion and conclusions

The results presented in this paper allow us to extend the analysis presented in our previous paper [19]. An analysis of the results given in Table 1 shows that the energies of the radical RA, both in the ground state and in the lowest excited state are much lower than those of a transition species for a purely intramolecular reaction between the stable form of DHP (I) and the molecule absorbing at 550 nm (III). This result may indicate that the initial step of the sequence of elementary processes following the excitation of the stable form of DHP (molecule I) is the formation of radicals rather than a purely intramolecular process assumed in earlier papers [1–19]. Indeed, the presence of paramagnetic species (radicals and/or triplets) has been confirmed by ESR measurements performed on irradiated polycrystalline DHP [24].

Admitting a possibility of the radical formation has its consequences for the postulated mechanism of the photochemical reactions. First, the recombination is a bimolecular process; in case of a geminate recombination (which seems to be the most likely case under experimental conditions reported in this paper), this should result in a second-order kinetics of the first step in the sequence of reactions. Secondly, the recombination may (at least in principle) proceed not only by the attachment of the phenyl in the position 3, but also in the positions 2 and 4 of the central ring, resulting in formation of the molecules III, I and VI, and consequently decreasing the yield of production of the coloured species III. Furthermore, one may ask whether, under favourable conditions, one could not expect also a non-geminate recombination of RA and phenyl (i.e., an intermolecular reaction). It seems, however, that both the formation of the molecule VI and an intermolecular reaction, though not impossible, seem to be of a lesser importance: earlier experiments [12,20,25,26] performed on 4,4-(biphenyl-2,2′-diyl)-2,6-diphenyl-1-methyl-1,4-dihydropyridine (BDH) showed that the latter molecule is photochromic in spite of the fact that the two phenyls in position 4 are linked with a chemical bond making impossible their complete separation from the central ring.

The shape of the decays measured in the experiments reported in this paper can be explained assuming a sequence of processes shown in Fig. 5. We postulate that the species absorbing at 520 nm is the molecule III in its ground and lowest triplet states, with the lifetime of the T_1 state being of the order of the time span of our measurements. We have been unable to unequivocally assign the experimental rate constants to postulated kinetic processes occurring in the samples after irradiation. Tentatively, we would attribute the slowest process to thermally driven chemical reaction(s).

The earlier measurements described in [13] revealed the existence of a more rapid process following the excitation of DHP, with the time constant amounting to ca. 20 μs. It should be pointed out that the latter decay was monitored at 390 nm, i.e., in the spectral range where one should expect an absorption from the RA radical. Thus, it is conceivable that the rate constant reported in [13] is that of the radical recombination in solution. Note, however, that the situation may be completely different in the solid state, where the lifetime of radicals may be much longer. The rate-determining process would be then the radical recombination; consequently, the kinetic analysis put forward in Section 3.2 would not hold.

The paths put forward in this paper do not contradict those proposed in our earlier paper [19], where the bleaching process was attributed to a 2,4-bridge formation (III → IV) or an intramolecular hydrogen shift (III → V), whereas closing processes in the photochromic cycle would correspond to the IV → III and/or V → III reactions, both photochemically driven. It is important to note at this point that, apart from the initial excitation of the parent DHP molecules resulting in the radical formation, the scheme shown in Fig. 5 takes into account thermally driven processes only. Thus the light-driven reverse processes IV → III and V → III, closing the photochromic cycle [19] have not been depicted in the figure. Moreover, our results show (cf. Fig. 4) that the concentration of coloured species in solution becomes close to zero after ca. 10 μs. This implies that the rates of thermally driven reverse reactions are negligibly small and may be neglected in the analysis.

Acknowledgements

This work was supported by the Polish State Committee for Scientific Research (grant No 3T9A4812) and by the Grant Agency of the Academy of Sciences of the Czech Republic (grant No A1050901). The authors thank Prof. J. Kuthan and Dr S. Böhm (Prague Institute of Chemical Technology) for the gift of the material used in the experiments decribed in this paper.

References

[1] K. Maeda, M. Nakamura, J. Photochem. 17 (1981) 87.
[2] K. Maeda, M. Nakamura, M. Sakai, J. Chem. Soc. Perkin Trans. 1 (1983) 837.
[3] F. Iwasaki, T. Watanabe, K. Maeda, Bull. Chem. Soc. Jpn. 60 (1987) 1255.
[4] J. Shibuya, M. Nabeshima, H. Nagano, K. Maeda, J. Chem. Soc. Perkin Trans. 2 (1988) 1607.
[5] Y. Mori, K. Maeda, J. Chem. Soc. Perkin Trans. 2 (1991) 2061.
[6] Y. Ohashi (Ed.), Reactivity in Molecular Crystals, Chap. 5, Kodansha and VCH, 1994, and references therein.
[7] J. Hašek, J. Ondráček, Acta Cryst. C46 (1990) 1256.
[8] S. Nešpůrek, W. Schnabel, J. Photochem. Photobiol. A60 (1991) 151.
[9] S. Nešpůrek, M. Schwartz, S. Böhm, J. Kuthan, J. Photochem. Photobiol. A60 (1991) 345.
[10] J. Vojtěchovský, J. Hašek, S. Nešpůrek, M. Adamec, Coll. Czech. Chem. Commun. 57 (1992) 1326.
[11] P. Šebek, S. Nešpůrek, R. Hrabal, M. Adamec, J. Kuthan, J. Chem. Soc. Perkin Trans. 2 (1992) 1310.
[12] S. Böhm, M. Hocek, S. Nešpůrek, J. Kuthan, Coll. Czech. Chem. Commun. 59 (1994) 263.
[13] S. Nešpůrek, W. Schnabel, J. Photochem. Photobiol. A81 (1994) 37.
[14] S. Böhm, P. Šebek, S. Nešpůrek, J. Kuthan, Coll. Czech. Chem. Commun. 59 (1994) 1115.
[15] S. Nešpůrek, S. Böhm, J. Kuthan, Mol. Cryst. Liq. Cryst. 246 (1994) 139.
[16] S. Böhm, M. Adamec, S. Nešpůrek, J. Kuthan, Coll. Czech. Chem. Commun. 60 (1995) 1621.
[17] H. Pirelahi, H. Rahmani, A. Mouradzadegun, A. Fathi, A. Moujoodi, J. Photochem. Photobiol. A101 (1996) 33.
[18] H. Rahmani, H. Pirelahi, J. Photochem. Photobiol. A111 (1997) 15.
[19] A. Lewanowicz, J. Lipiński, S. Nešpůrek, A. Olszowski, E. Śliwińska, J. Sworakowski, J. Photochem. Photobiol. A121 (1999) 125.
[20] J. Sworakowski, S. Nešpůrek, M. Bertault, Mol. Cryst. Liq. Cryst. 313 (1998) 199.
[21] M.J.S. Dewar, W. Thiel, J. Am. Chem. Soc. 99 (1977) 4899.
[22] J. Lipiński, Int. J. Quant. Chem. 34 (1988) 423.
[23] J. Lipiński, unpublished results.
[24] A. Lewanowicz, J. Lipiński, J. Sworakowski, M. Komorowska, S. Nešpůrek, in: Proc. Int. Workshop on Reactive Intermediates (IWRI '99), Szczyrk, Poland, 1999.
[25] J. Sworakowski, S. Nešpůrek, J. Lipiński, A. Lewanowicz, E. Śliwińska, Mol. Cryst. Liq. Cryst., submitted for publication.
[26] E. Śliwińska, J. Sworakowski, in preparation.