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Kinetics of Photochromic Processes in Substituted Dihydropyridines in the Solid State and in Solutions

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Results are presented of studies of the kinetics of thermally driven reactions in substituted dihydropyridines: 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (DHP), and 4,4-(diphenyl-2,2′-diyl)-2,6-diphenyl-1-methyl-1,4-dihydro-pyridine (BDH). The processes have been monitored by measuring the isothermal bleaching of coloured species produced upon UV irradiation of the samples, and by measuring the heat flow in non-isothermal differential scanning calorimetry experiments. 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 may be a radical, the absorption at 520 nm being probably associated with S_0 and T_1 states of one of intermediate products. 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. The results described above are compared with those obtained on BDH – an analogue of DHP in which the potentially mobile phenyl groups are linked with a chemical bond.

Keywords: dihydropyridine; photochromism; reaction kinetics

INTRODUCTION

Photochemical properties of derivatives of dihydropyridines, pyranes, and thio- and selenopyranes 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 [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 (see Fig. 1; hereafter referred to as DHP). The absorption spectra of the stable and coloured forms of solutions and polycrystalline samples of DHP are essentially identical, the similarity indicating that the same species are involved in the photochemical processes in both cases.

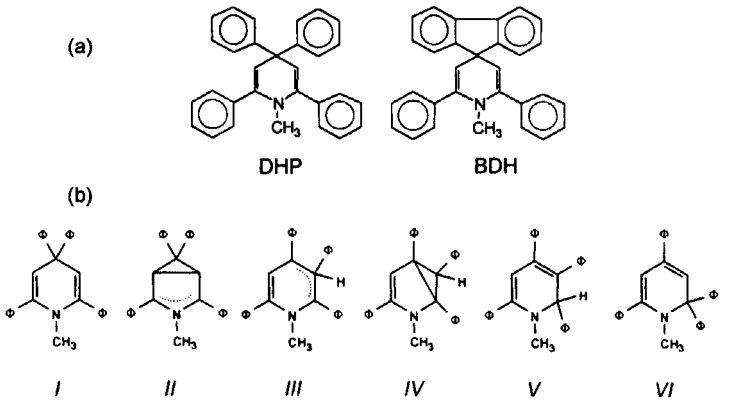

FIGURE 1. *(a)* Chemical formulae of the stable forms of DHP and BDH. *(b)* Possible metastable species (*II-VI*) formed upon illumination of DHP.

The stable form of DHP has its long-wavelength absorption edge in the near UV, irradiation into its UV absorption band giving rise to a build-up of additional 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]. Experiments performed on solutions of DHP [13] clearly indicate the first-order character of the 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].

Much less information has been accumulated for 4,4-(biphenyl-2,2'-diyl)-2,6-diphenyl-1-methyl-1,4-dihydropyridine (BDH) – an analogue of DHP in which the potentially mobile phenyl groups are linked with a chemical bond (cf. Fig.1a). The material also exhibits photochromic properties, with the absorption band appearing after the illumination at ca. 640 nm [15,20].

The aim of the present contribution is to put forward results of the measurements of the kinetics and energetics of the reverse reaction in DHP and BDH. We carried out measurements of the bleaching processes employing isothermal and non-isothermal techniques. Results of our experiments, supplemented with quantum-chemical calculations, allowed us to identify the products and to put forward the reaction paths.

EXPERIMENTAL

The measurements reported in this paper were carried out on samples supplied by Prof. J. Kuthan and Dr S. Böhm (Prague Institute of Chemical Technology). The details of synthesis, purification and characterization of the materials were described elsewhere [9,11,12].

The polycrystalline samples were irradiated with a UV lamp supplied with a bandpass filter shining into the UV absorption bands of the materials. UV-VIS spectra and the kinetics of isothermal bleaching were determined from direct measurements of the absorption of polycrystalline DHP and BDH in KBr matrices. The DSC measurements were carried out employing a Perkin Elmer DSC7 scanning calorimeter, between ca. 250 K and a temperature ca. 5 K below the respective melting point.

The kinetics of bleaching reaction of oxygen-free solutions of DHP and BDH was studied using a conventional flash-photolysis setup similar to that described elsewhere [13]. The samples were excited with a 15 ns pulse from a frequency-quadrupled Nd:YAG laser (λ= 266 nm); the bleaching kinetics was then measured by following the decay of the

absorption band in the visible. Typically, the time span of the measurements reported in this paper amounted to 5–10 ms for DHP, and ca. 10 μs for BDH.

RESULTS

Quantum-chemical calculations

The calculations reported in this paper were carried out in order to determine the geometries of the stable forms of DHP and BDH, geometries of possible intermediate and final products of photochemical reactions (cf. Fig. 1), and of transition species between the products. We also carried out calculations of a radical formed from the stable form of DHP (molecule *I*) by breaking the C(4)-phenyl bond. Furthermore, calculations of the energies of the ground and low-lying excited states of the reactants, 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 optimized using the semiempirical MNDO method of Dewar and Thiel [21]. The excitation energies and reaction paths in the excited state were calculated using the semiempirical GRINDOL method [22], particularly suitable in this type of calculations. The energies of the ground and lowest excited states of all species involved in the photochromic cycles of DHP and BDH are given in Table 1.

Crystalline materials

Irradiation of the polycrystalline materials results in the appearance of coloured forms, their absorption maxima located at ca. 550 nm (DHP) and 640 nm (BDH) – cf. Fig. 2. The isothermal kinetics of the bleaching reactions can be followed as a decrease of intensities of the bands in the visible region; earlier experiments (e.g., [8,19]) showed that the decays are reasonably described by the 'stretched exponential' function, with temperature-dependent parameters: ambient-temperature rate constants were of the order of hours, and the average activation energies amounted to ca. 37 kJ/mol.

The calorimetric measurements performed on the samples irradiated with UV revealed exothermic anomalies at elevated temperatures. The effect could be observed only once: subsequent runs

TABLE 1. Energies of the ground states and the lowest excited states in DHP and BDH. The symbols denoting the molecules are identical as in Fig. 1. All values are given in kJ/mol, relative to the energies of the ground states of the stable forms of DHP and BDH, respectively.

Molecule		Ground and lowest excited states of molecules			Ground and lowest excited states of radical	
		S_0	T_1	S_1	Ground state	Excited states
Stable and metastable molecules (cf. Fig. 1)						
I	DHP	0	290	402		
	BDH	0	298	408		
II	DHP	92		373		
	BDH	134		427		
III	DHP	29	48	247		
	BDH	92		302		
IV	DHP	17	306	465		
	BDH	55		453		
V	DHP	-59	167	293		
	BDH	-17		298		
VI	DHP	19		377		
Transition species for purely intramolecular reaction						
(I-III)	DHP	335	318	457		
	BDH	360		432		
(I-II)	DHP	306		612		
	BDH	163		490		
(III-IV)	DHP	71	113	305		
	BDH	113		373		
(III-V)	DHP	117	147	344		
	BDH	126		432		
(III-VI)	DHP	298		401		
	BDH					
Radical (RA + phenyl)						
RA	DHP				177	309; 456

performed on the same samples were qualitatively different, the difference being associated with heat evolved during thermally driven reverse reactions occurring between the metastable and stable forms of the photochromic systems. Our results demonstrate that the temperature dependence of the excess heat flow (the difference of the heat flows measured during the first and the second run) is a function of the

conditions of irradiation. A detailed study performed on DHP was described elsewhere [19]: depending on the irradiation conditions, we could observe the presence of two peaks with different build-up times, apparently associated with two different processes. The technique of 'Fractional Heating' [23] yielded the activation energy of the high-temperature process amounting to (130 ± 30) kJ/mol.

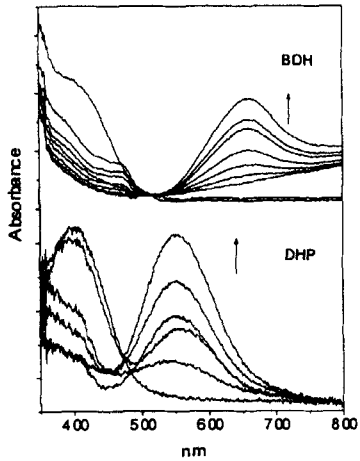

FIGURE 2. Temporal evolution of the absorption spectra of the polycrystalline materials under study during UV irradiation. The maximum irradiation times amount to 180 minutes; the arrows indicate the direction of the build-up of the visible absorption band.

Results of the calorimetric experiments performed on BDH are shown in Fig. 3. Qualitatively, the results are similar to those obtained for DHP, indicating that the processes leading to the photochromic behaviour should be of a similar nature. A quantitative analysis of the results is, however, difficult due to a feature appearing above ca. 320 K, associated probably with a phase transition in BDH or in one of the products of the photochemical cycle. The activation energy obtained from a series of measurements amounts to ca. (140± 40) kJ/mol.

Kinetics of bleaching in solutions

A typical decay of the absorbance at 520 nm, measured in a diluted solution of DHP in chloroform, is shown in Fig. 4. The curves were found to consist of an initial section of a rapid decay, separated from a slower decay by a plateau around 0.8–1.5 ms. In our previous paper [19], we attributed the decays to two parallel processes; the 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 around 520 nm.

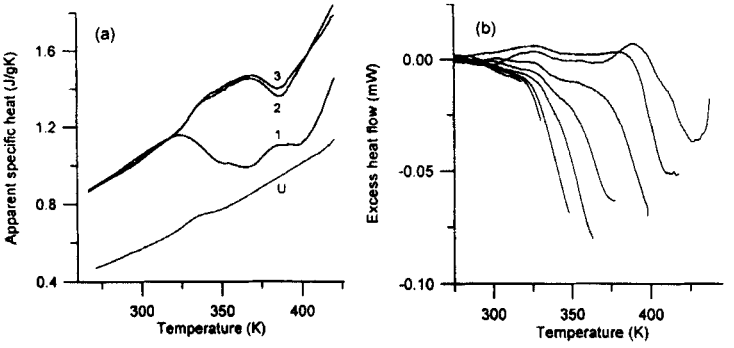

FIGURE 3. DSC experiments on BDH. (*a*) Apparent specific heat measured on an unirradiated sample (labelled 'U', displaced), and on a sample irradiated with UV. The numbers indicate the sequence of DSC runs following the irradiation. (*b*) The fractional heating experiment.

Taking into account results of the quantum-chemical calculations, we put forward a simplified sequence of elementary reactions as shown in Fig. 5 (see also [24]). The model presented in [24] modifies initial stages of photochemical processes following the excitation of DHP. 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 molecule *I*, and/or in formation of the coloured species (molecule *III*), and, possibly, also of a molecule *VI*. 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 [24] indicate that the optical gaps for the $S_0 \rightarrow S_1$ and $T_1 \rightarrow T_2$ absorption are quite close (18000 cm^{-1} *vs.* 20700 cm^{-1}).

The scheme shown in Fig. 5 can be solved for the concentrations of the relevant products (the *RA* radical, and the ground- and triplet state forms of *III*) [24]; the resulting equation reads

$$A = \alpha \exp(-k_X t) + \beta \exp(-k_{DG} t) - \gamma \exp(-k_{DX} t), \qquad (1)$$

where A stands for the absorbance normalized to its initial value, α, β and γ are time-independent parameters, and k_X, k_{DG} and k_{DX} are combinations of rate constants of the elementary processes.

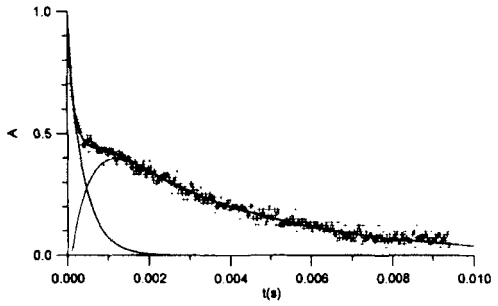

FIGURE 4. Ambient-temperature bleaching kinetics of DHP in chloroform. Thin full lines show temporal evolutions of absorbances of products, the thick line is the reconstructed curve calculated using Eq. (1) and the rate constants determined from the fit.

The shape of the decays measured in the experiments reported in this paper can be well fitted with Eq. (1) resulting from sequence of processes shown in Fig. 5. We therefore 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 of the order of the time scale of our experiments.

The time constants determined from the experimental curves amount to (5000±1000) s^{-1}; (500±100) s^{-1} and (1500±500) s^{-1}. A poor reproducibility of the results does not allow us to unequivocally assign the experimental rate constants to postulated kinetic processes occurring in the samples after irradiation. Tentatively, we attributed the slowest process to thermally driven chemical reaction(s).

The measurements performed on chloroform solutions of BDH cover at the moment only the microsecond range. We noticed a pronounced dependence of the shape of decays on the monitoring wavelength but the preliminary character of the results obtained so far does not allow us to draw any far-reaching conclusions.

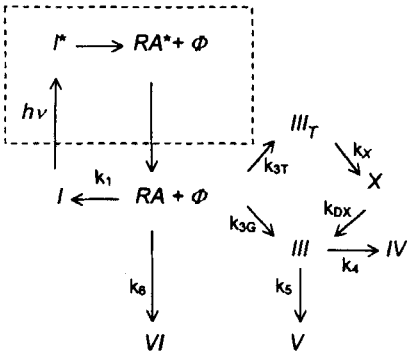

FIGURE 5. The proposed sequence of elementary processes in DHP following a UV pulse. The symbols denoting molecules are those used in Fig. 1, *RA* is a radical, and *X* is an intermediate product. The processes inside the box occur beyond the time scale of the experiment.

ESR measurements

Presence of paramagnetic species has been additionally confirmed by ESR experiments [25]. In this section we present only preliminary results of ESR measurements performed on pre-irradiated DHP samples. As the time constants of processes occurring in solutions were much shorter than those required for reliable measurements on the available equipment, the measurements were carried out on polycrystalline samples where the kinetics of bleaching was found much slower (see the preceding sections).

Figure 6 shows the ESR spectrum of a sample irradiated with UV light, compared to that of a pristine sample. Two broad peaks can

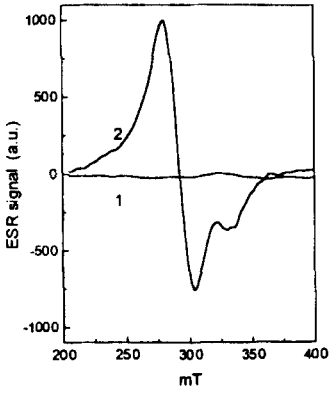

FIGURE 6. ESR signal measured in a polycrystalline DHP: sample. 1 – pristine sample; 2 - the same sample after irradiation with UV.

be identified, characterized by their g factors and widths amounting to 2.2(9) and 0.032 T, and 2.0(2) and 0.013 T, respectively. A detailed analysis of the results obtained is beyond the scope of this paper; the results presented here serve only to support our analysis providing an evidence for the existence of metastable paramagnetic species which are produced by irradiation of DHP.

FINAL REMARKS

Basing on results of spectroscopic measurements, isothermal and non-isothermal kinetic experiments, as well as on results of quantum-chemical calculations, we put forward a scheme explaining the photochemical activity of substituted dihydropyridines. Our results indicate that the initial step of the sequence of elementary processes following the excitation of the stable form of DHP (molecule *I*) may be the formation of radicals rather that a purely intramolecular process assumed in earlier papers [1-19]. A possibility of the radical formation has its consequences for the postulated mechanism of the photochemical reactions. In particular, one may ask whether, under favourable conditions, one could not expect also a non-geminate recombination of *RA* and phenyl (i.e., an *inter*molecular 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: our experiments performed on 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.

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