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Differential scanning calorimetry in studies of solid-state reactions in photochromic materials

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Abstract

Differential scanning calorimetry (DSC) was employed to study the kinetics of reverse thermally driven reactions in polycrystalline samples of three photochromic compounds. Results obtained on two dihydropyridine derivatives were critically re-examined and compared with results of the experiments performed with an acridizinium salt. Heat flow curves, measured on samples previously irradiated with UV, exhibited broad exothermic anomalies at elevated temperatures (above ca. 320 K for dihydropyridines and above ca. 490 K for the acridizinium salt), observed only once after irradiation and attributed to bleaching reactions. The activation energies of bleaching reactions in the dihydropyridine derivatives, determined from fractional heating experiments, amount to ca. 90–170 kJ/mol. Exact determination of the distribution of activation energies proved difficult due to uncertainties with a proper setting of baselines.

Keywords: Photochromism; Differential scanning calorimetry; Dihydropyridine; Acridizinium; Kinetics; Solid state reaction

1. Introduction

Among a large number of photochromic systems investigated so far (cf., e.g., [1,2]), few have been found to be photochromic in the crystalline state. Photochromic organic crystals are interesting not only as potential novel materials for optical data processing and storage; it is expected that photoinduced molecular transformations might be used to gain control over other physical properties in the solid state [3]. Rate constants of forward (photochemically driven) and reverse (thermal and/or photochemical) processes are among fundamental parameters characterising photochemical activity of photochromic compounds. These parameters are often determined from isothermal measurements performed at several temperatures, usually employing spectroscopic methods. In some cases the isothermal methods can be supplemented with (or even replaced by) methods operating in a non-isothermal regime [4]. Use of non-isothermal methods allows one to gain, in principle, the same kinetic information from a single run, the latter feature becoming particularly important if samples under study undergo irreversible side reactions.

One of non-isothermal techniques which may be employed in studies of crystalline photochromic systems is the differential scanning calorimetry (DSC). In previous papers of the present authors, use of DSC in studies of thermally driven reactions was discussed [5], and its applicability to determine kinetic parameters in polycrystalline photochromic dihydropyridine derivatives was demonstrated [6–8]. It was shown that DSC, used together with other experimental methods and quantum-chemical calculations, may yield valuable results allowing one to determine reaction paths in complex photochromic cycles. The calorimetric technique also provides information about the enthalpy of reactions occurring in the materials under study, and hence allows one to gain information about relative position of the ground states of the reactant and product.

The results reported in our previous papers [6–9] were obtained on materials which will also be used in the experiments described in the present paper: 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine and 4,4-(biphenyl-2,2′-diyl)-2,6-diphenyl-1-methyl-1,4-dihydropyridine (hereafter referred to as DHP and BDH, respectively—cf. Fig. 1). A sequence of reactions following UV irradiation of dihydropyridine derivatives appeared to be quite complex [7,9] (see Fig. 1b). A comparison of results obtained from experiments performed on DHP molecules dissolved in liquid solvent or in polymer matrices [10] with those obtained on

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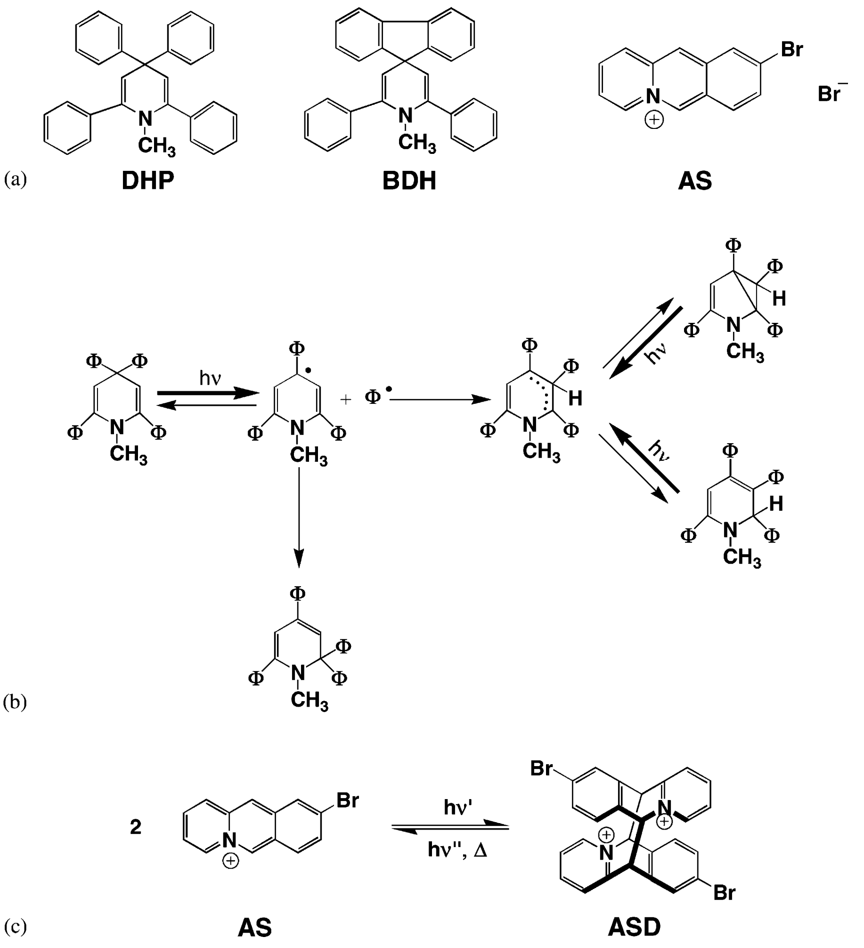

Fig. 1. (a) Chemical formulae of the stable forms of photochromic materials under study. (b) A simplified scheme of postulated reactions following UV excitation of DHP [7,9]. (c) The photochromic cycle in AS.

polycrystalline DHP samples demonstrated dramatic differences in the kinetics of bleaching reactions, thus pointing to an important role of the environment. Our earlier experiments [6–9] indicate that at least two processes are responsible for the bleaching; moreover, fractional heating experiments (see infra) yielded results which in some cases disagreed with theoretical predictions [5]. Thus is seemed reasonable to critically re-examine results obtained from the DSC measurements.

This contribution reports on measurements of the kinetics and energetics of thermally driven bleaching reactions in polycrystalline samples of dihydropyridine derivatives supplementing our earlier research performed using UV–Vis and NMR spectroscopy, and quantum-chemical calculations [6–9,11]. For comparison, we also performed DSC measurements on another photochromic system, namely 9-bromoacridizinium bromide AS [12], whose irradiation leads to the regioselective formation of the anti-head-to-tail dimers ASD exclusively either in the single crystal or in the polycrystalline state [13]. Moreover, acridizinium dimers may be reverted to the monomers on heating [14]. This photochromic system appears to be simpler than that in dihydropyridine derivatives, involving only a formation and cleavage of C–C bonds between the meso positions of a pair of neighbouring molecules (c.f. Fig. 1c). Moreover, the conversion of the photodimerization of AS in the solid state was shown to be 95% at least [13].

2. Experimental

Details of the synthesis and purification of the materials under study have been described recently [12,13,15]. The measurements were carried out with a Perkin Elmer DSC 7 differential scanning calorimeter. The temperature scale of the calorimeter was calibrated with the melting points of high-purity indium (429.72 K), cyclohexane (279.72 K) and *m*-dinitrobenzene (362.69 K) at the same heating rate as that used in the experiments (10 K/min). The purge gas was nitrogen at the flow rate of 1 dm^3/h. The DSC scans were run on polycrystalline samples powdered directly before the experiments and irradiated with an Emita VP60 UV lamp supplied with a cut-off filter eliminating most of the visible light. The samples were then sealed in aluminium pans, with an empty pan used as reference. Masses of the samples amounted to 10–30 mg, the irradiation time ranging between 15 and 180 min.

In single-run experiments, the samples were heated from a starting temperature (typically 260 K) to a temperature a few degrees below the melting points of the materials under study (the end points of our experiments were 440 K for DHP and BDH and 520 K for AS, whereas their respective melting points amount to 455 K (DHP), 456 K (BDH) and 540 K (AS)). At least two runs were performed on each sample under identical conditions, the curve recorded during the last run serving as a baseline.

Bearing in mind the results of the isothermal measurements [6,10] which indicate that the kinetics of the reverse process (bleaching) is probably controlled by distributions of the rate constants, we employed the technique of fractional heating DSC [5]. The method, similar to that often employed in studies of dipolar relaxation in dielectrics [16,17], allows one to separate possible independent processes and to gather information about a distribution of activation energies. In fractional heating experiments, sequences of heating runs were recorded, starting at a low temperature (here at 260 K), terminating at progressively increasing temperatures, and followed by a rapid cooling to the initial temperature (cf. insert of Fig. 4). The baselines for fractional heating experiments were recorded after the samples had been heated to the highest temperatures.

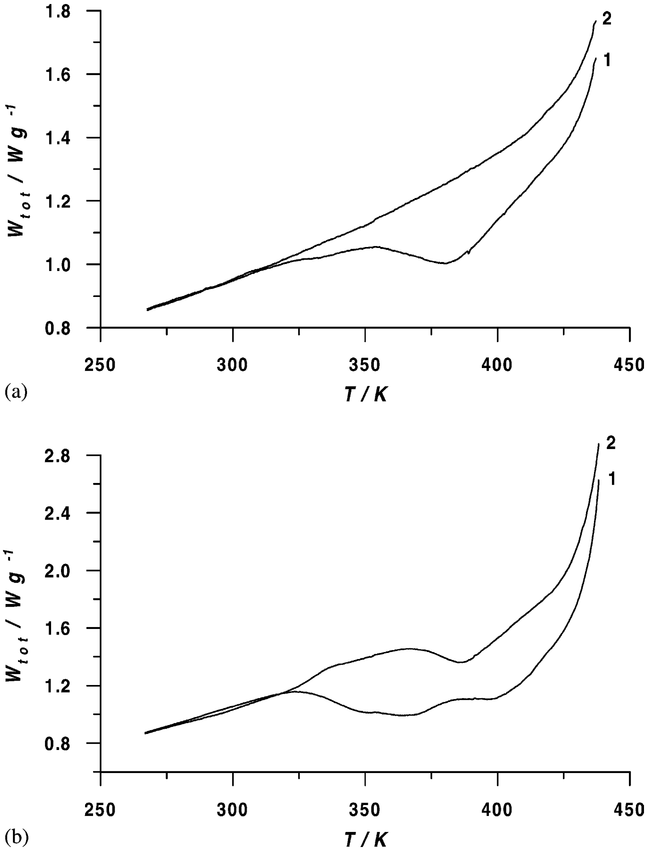

Fig. 2. Typical single-run experiments on DHP (a) and BDH (b). 1: A run carried out on a sample irradiated with UV light; 2: a second run carried out immediately after the first one.

3. Results

3.1. Dihydropyridine derivatives

Results of typical single-run experiments performed on DHP and BDH are shown in Fig. 2. All experiments yielded qualitatively the same picture: heat flow curves recorded on samples immediately after their exposure to UV radiation exhibited exothermic anomalies starting above ca. 300 K. The anomalies were absent in second (and all following) runs performed on the same samples. Assuming that the specific heat of the sample does not significantly change during the experimental cycle (reliability of this assumption will be assessed later), the difference between the first and any subsequent heating run (hereafter referred to as excess heat flow W_r) should be solely associated with a chemical reaction occurring in the sample; we attributed it to bleaching reaction(s) involving metastable (coloured) species.

We also attempted to determine the magnitude of the DSC response on the irradiation time. Dependence of the shape of the excess heat curve in DHP on the irradiation time

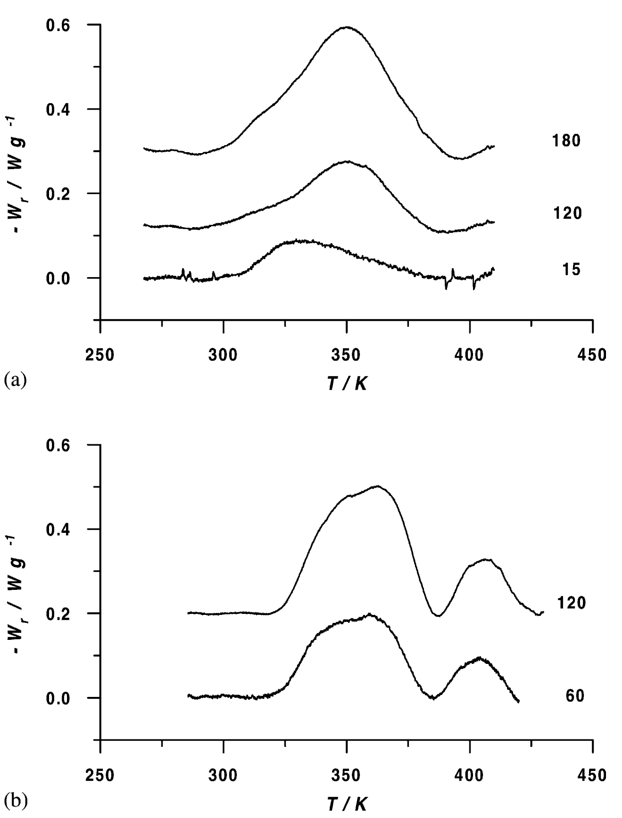

Fig. 3. Dependence of the shape of the excess heat flow on the irradiation time in DHP (a) and BDH (b). The parameter is irradiation time in minutes. The curves have been vertically displaced.

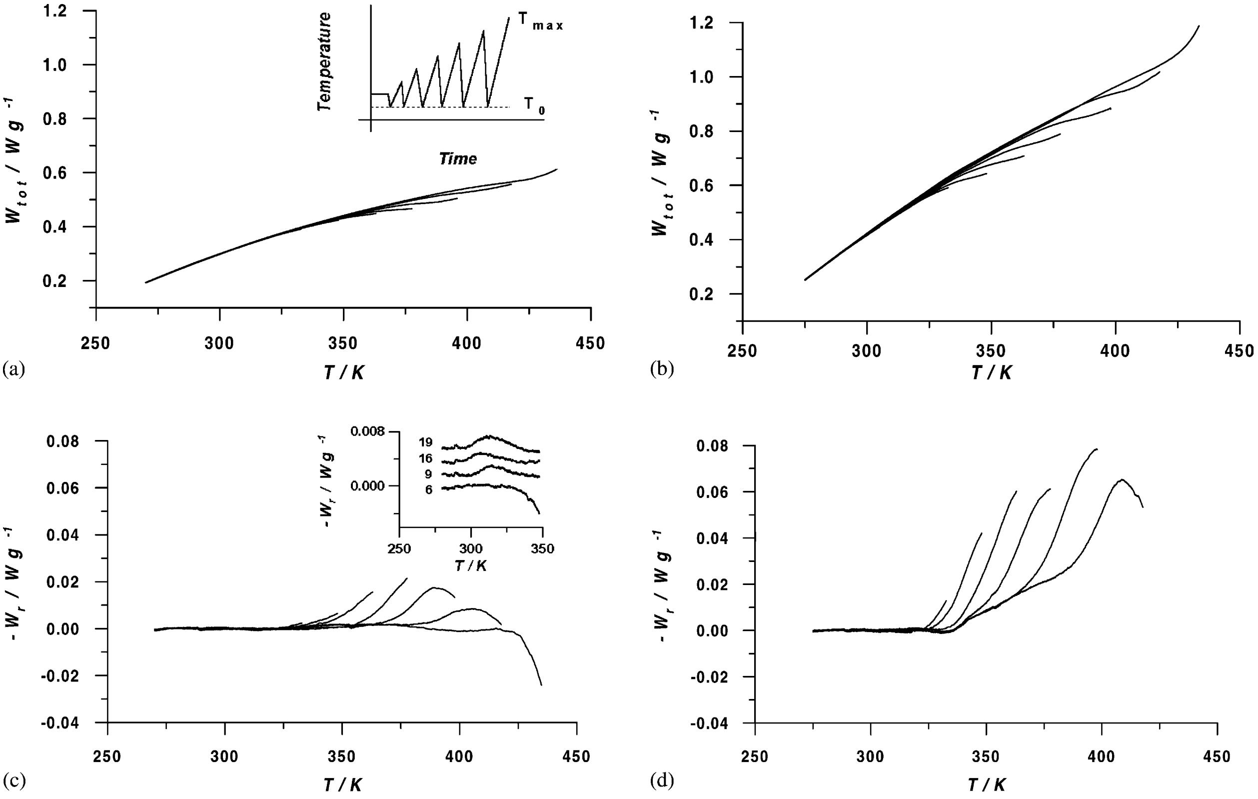

Fig. 4. Fractional heating DSC experiments on DHP (a, c) and BDH (b, d). Total heat flows measured in series of heating runs following irradiation of samples (a, b) and the excess heat flows calculated after subtracting baselines (c, d). The numbers in (c, d) indicate the sequences of experimental runs. Insert in (a): a typical temperature–time programme during a fractional heating experiment, following the irradiation of a sample; insert in (c) expanded fragments of excess heat flow curves demonstrating a build-up of a persistent endothermic peak around 300–320 K. Only the 6th, 9th, 16th and 19th runs are shown; the curves have been vertically displaced.

is shown in Fig. 3a. The main feature of the curves measured on samples irradiated for 15 min is a peak at ca 330 K, which, in samples irradiated over longer times, merges into a growing dominating feature peaking above 360 K. Excess heat flow curves measured on BDH exhibit the presence of two well-separated peaks, irrespective of the irradiation time (Fig. 3b).

Results of typical fractional heating experiments performed on polycrystalline DHP and BDH samples are shown in Fig. 4. A fit to the excess heat flow curves with the Arrhenius equation should yield the activation energies (and their distributions). We encountered, however, problems with setting baselines, influencing the results obtained (see infra).

3.2. 9-Bromoacridizinium bromide (AS)

Only single-run experiments were performed on polycrystalline samples of the acridizinium salt dimer ASD. We observed an exothermic anomaly becoming discernible at ca. 480 K and peaking at 500 K (cf. Fig. 5). The anomaly was observed only once, thus the excess heat could be attributed to the reverse reaction of the photochromic cycle (bond cleavage—cf. Fig. 1c). This assumption was confirmed by independent thermolysis of authentic solid samples of ASD at 240 °C and subsequent analysis of the reaction mixture by ^{1}H-NMR spectroscopy and comparison with reported NMR data [13a]. Thus, 2 min of thermolysis already gave 14% yield of the monormer AS, and after 5 min, 33% of the monomer were present in the reaction mixture. This result confirms that at these temperatures, the acridizinium dimer reverts back to the monomer.

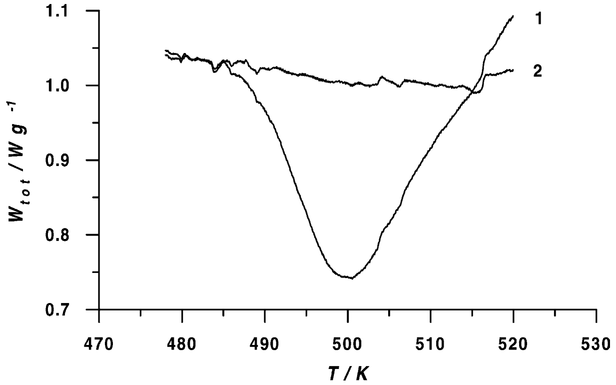

Fig. 5. A single-run experiment on a solid sample of ASD. The numbers indicate the sequence of runs.

4. Discussion

The single-run experiments carried out on DHP and BDH should, in principle, allow for a separation of possible independent processes and provide information about the reaction enthalpies. In DHP, we could indeed observe a superposition of two exothermic features, exhibiting different dependences on the irradiation time (cf. Fig. 3a). The effect observed points to a co-existence of two independent bleaching processes. A situation in BDH seems more complex: we found two peaks on the excess heat flow curves (see Fig. 3b), hence one may postulate a co-existence of two bleaching processes as well. However, on inspecting the total heat flow curves we noticed persistent endothermic anomalies above 350 K appearing in particular on the second (and subsequent) runs, possibly pointing to the existence of a phase transition in an (unidentified) product. The presence of the anomaly makes difficult a reliable setting of the baseline. Consequently, we could not unambiguously decide whether the peak appearing above 400 K on the excess heat flow curve (Fig. 3b) is associated with a second bleaching process or whether it is an artefact due to a transition occurring in a product of the photochemical reaction of BDH. It should also be noted that similar anomalies, probably due to traces of some impurities present in our samples, were detected in pristine (unirradiated) BDH [8].

Integration of the heat flow curves should yield the total enthalpy of bleaching process(es). Unfortunately, we were unable to determine the conversion of DHP and BDH into coloured products, thus no quantitative determination of ΔH_r of the reverse reaction was possible. Apparent enthalpies of the reverse processes (calculated for complete conversions) yielded the values ranging between -5 and -1.5 kJ/mol. It should be realized, however, that these numbers are lower estimates compared to the actual values which may be an order of magnitude larger. In contrast to dihydropyridines, the degree of conversion of AS into the photodimer is known to amount to ca. 95% [14]. It allowed us to determine the enthalpy of the cycloreversion reaction occurring in polycrystalline samples of the acridizinium dimer: an average value of ΔH_r amounted to -1.75 kJ/mol. As the melting of the samples was accompanied by their decomposition, precautions had to be taken to ensure reliable measurements. Moreover, this value is likely to be underestimated as the end of the exothermic anomaly seems to coincide with an onset to pre-melting effects (cf. Fig. 5). In fact, the reaction enthalpy of the thermal transformation of the unsubstituted acridizinium dimer to the monomer was reported to be -78 kJ/mol on the basis of heat-of-combustion measurements [14b]. However, in contrast to our experiments the heat of combustion was apparently determined from a mixture of four regioisomeric dimers.

It was mentioned in the preceding sections that the analysis of fractional heating runs should allow for a determination of activation energies (and of their distributions) of bleaching processes. The model calculations reported in [5] demonstrate that the activation energies in a series of partial heating runs to progressively higher temperatures should either increase of remain constant, depending on the distribution. Results obtained on some polycrystalline DHP samples seemed to contradict this conclusion: the activation energies were found to *decrease* (cf. Fig. 6); moreover, the activation energies calculated from the curves measured on several samples exhibited a large spread. An explanation of the apparent discrepancies is based on analysis of several runs performed on 10 samples.

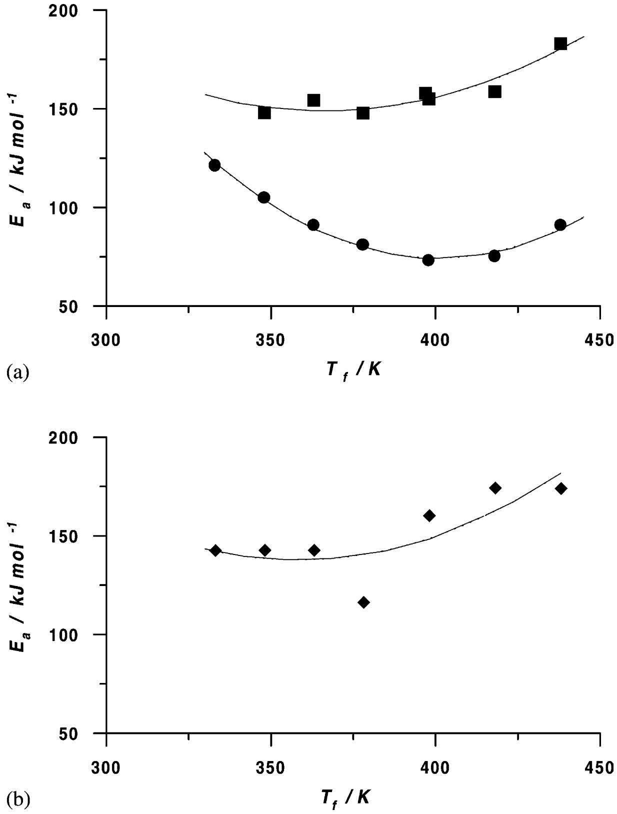

Fig. 6. (a) Two types of dependences of the activation energy on the end temperature in fractional heating experiments performed on DHP samples. The results obtained on two different samples are shown; results for other DHP samples are qualitatively similar to either of the dependences displayed. (b) A dependence of the activation energy on the end temperature in a fractional heating experiment performed on BDH sample.

The photochemical reactions occurring in crystalline dihydripyridine derivatives are space-demanding, hence their kinetics depends critically on the perfection of samples [18]. Thus the effect measured in a superposition of contributions coming from molecular and environment-dependent processes. A rapid thermal cycling employed during fractional heating experiments is likely to result in cracking of the crystallites, the latter process depending on several ill-defined and ill-reproducible factors. Thus one may expect the environment-dependent part of the activation energy to differ from sample to sample and even to decrease as has indeed been observed in our experiments.

Another factor contributing to the spread of the activation energies seems to be a build-up of persistent features, which we tentatively attribute to a signature of a phase transition occurring in an unidentified product. A similar feature was observed in BDH (see above); in DHP its formation is slower but discernible after several runs performed during a partial heating experiment (see insert to Fig. 4c). Therefore, the presence of the endothermic peak does not affect single-run experiments performed on DHP but is influence cannot be neglected in partial heating experiments. Moreover, the activation energies determined from the fractional heating curves may be burdened with yet another error: the Arrhenius plot yields reliably rectilinear dependences only in the initial parts of each curve which, on the other hand, are deformed by a background noise, possible errors in setting the background curve etc. In this case the choice of fitting limits, always arbitrary to some extent, results in increasing the scatter of activation energies calculated from the fits.

Our results do not allow us to draw quantitative conclusions regarding parameters characterizing a possible distribution of activation energies in polycrystalline DHP. The average value obtained from the initial fractional heating curves amounts to (130 ± 40) kJ/mol (cf. Fig. 6a) but the scatter of the energies determined from further runs on different samples makes impossible any further analysis.

Due to a limited amount of available crystalline BDH, only a few fractional heating experiments were performed. A representative result is shown in Fig. 6b. It should be noted that, contrary to the situation in DHP, we did not observe any decrease of the activation energy in the consecutive runs.

A question arises whether activation energies determined from the experiments reported in this paper can be compared with barrier heights calculated employing quantum-chemical methods [7,9]. In most cases, the experimental values exceed those obtained from the calculations. The discrepancy can be reasonably explained by taking into account differences in the molecular environment. The calculations have been carried out for isolated molecules whereas the experiments have been performed on polycrystalline samples, in which the kinetics is dependent on the environment, presence of defects, conditions of experiments, etc., as was discussed above. One may therefore expect that the lowest experimental activation energies determined on polycrystalline samples should be the closest to respective molecular values.

5. Conclusions

The aim of this paper was to re-examine the use of the DSC technique in to studies of the kinetics and energetics of solid-state reactions following UV illumination of photoactive materials. We studied reverse reactions of the photochromic processes in polycrystalline samples of DHP, BDH and AS. In all irradiated samples of systems under study we observed broad exothermic anomalies on their heat flow curves, attributed to thermally driven reverse reactions from the metastable to the stable form (bleaching reaction). We believe to have demonstrated that, properly used, the method yields results supplementing those obtained from other experimental methods and from quantum-chemical calculations. One should nevertheless consider that the results must be critically assessed, as they are likely to be obscured by factors not related to the processes under investigation.

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