DETERMINATION OF THE QUANTUM YIELDS OF PHOTOCHEMICAL REACTIONS BY MEANS OF ABSORPTION SATURATION MEASUREMENTS
I: QUANTUM YIELDS OF PHOTOCHEMICAL INTRAMOLECULAR PROTON TRANSFER REACTIONS IN 2-(2',4'-DINITROBENZYL)-PYRIDINE SOLUTIONS

J. KLEINSCHMIDT and A. GRANESS

Physics Department, Friedrich Schiller University Jena, 6900 Jena (G.D.R.)

Summary

The quantum yields of intramolecular photochemical reactions were determined by means of absorption saturation measurements. The methods described enable the reaction quantum yields to be determined absolutely without a knowledge of the absorption cross sections or the concentrations of the transients produced photochemically. The methods are based on irradiation by intense nanosecond or picosecond pulses into the $S_0 \rightarrow S_1$ transition of the photochemically formed transient which results in absorption saturation of this transition. The concentration of this transient and the absorption cross section of the $S_0 \rightarrow S_1$ transition can be calculated from the experimentally determined intensity-dependent transmission of the light pulses.

1. Introduction

The coloured form of 2-(2',4'-dinitrobenzyl)pyridine (2-DNBP) which is produced by a reversible photochemical reaction has a polymethine structure [1]. Results of previous investigations have shown that the *aci*-nitro form of 2-DNBP is formed as an intermediate in both polar and non-polar solvents. This intermediate undergoes a thermal reaction in the ground state to give the polymethine structure which is formed by intramolecular proton transfer from the oxygen of the *aci*-nitro group to the nitrogen of the pyridine group [2]. Wettermark and Sousa [3] determined the quantum yields of the photochromic reaction of 2-(2-nitro-4-cyanobenzyl)pyridine at excitation wavelengths of 254 nm and 365 nm and found $\phi_{254} = 0.032$ and $\phi_{365} = 0.014$. The absorption cross section of the coloured form was determined by assuming complete conversion of the colourless compound to the coloured form.

In this paper we describe nanosecond and picosecond absorption saturation experiments which were performed to determine the absorption cross section of the $S_0 \rightarrow S_1$ transition of the coloured polymethine form

(CPF). The calculation of the quantum yields is possible without making any assumptions about the concentration of CPF in the solution.

2. Experimental details

2.1. Materials

The two compounds investigated are shown in Fig. 1.

2-DNBP and the azamerocyanine of N-methyl-2-(2',4'-dinitrobenzyl)-pyridinium iodide (CH$_3$-DNBP) were synthesized and purified by Klemm and
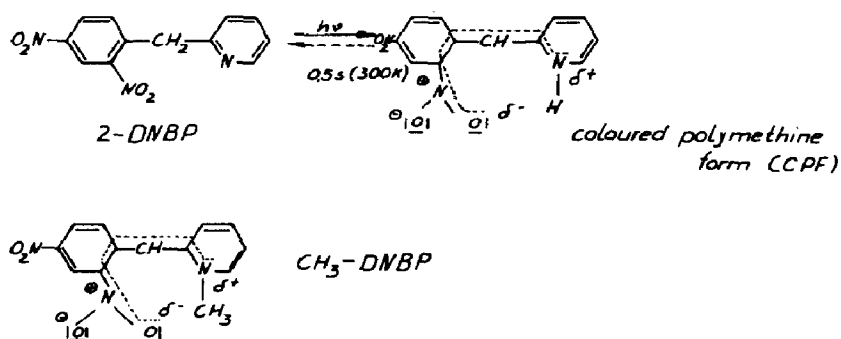

Fig. 1. Structures of the compounds investigated.

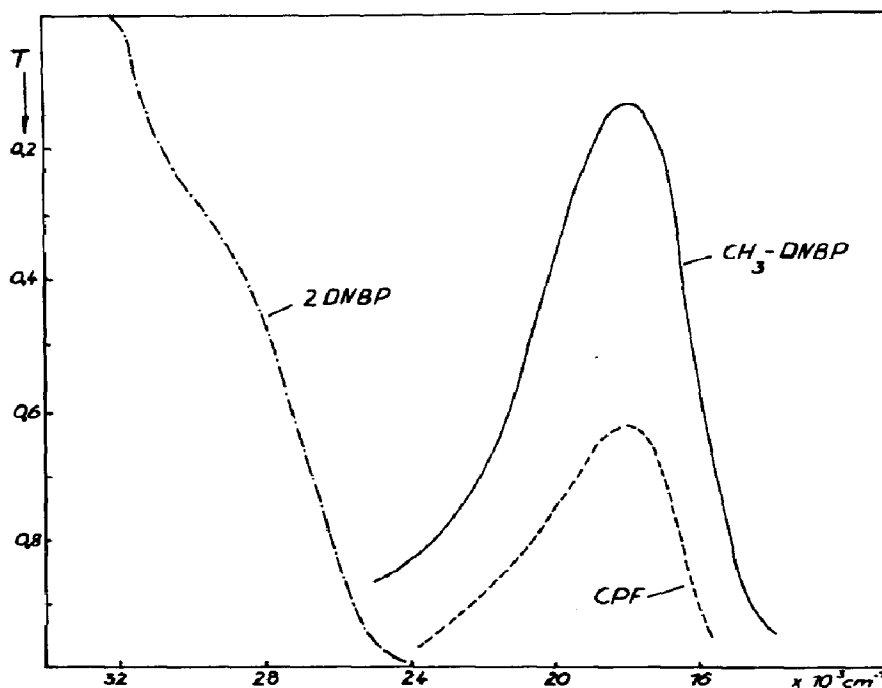Fig. 2. Absorption spectra of 2-DNBP (1×10^{-3} mol l^{-1}), CH$_3$-DNBP (4.6×10^{-5} mol l^{-1}) and the transient absorption spectrum of photochemically produced CPF (2-DNBP concentration, 1×10^{-3} mol l^{-1}; excitation energy per pulse, about 50 mJ) in ethanol at room temperature (cell length, 1 cm).

Klemm [1, 4]. The purity of these compounds was checked by thin layer chromatography and elementary analysis. The ethanol solvent was purified according to standard procedures.

CH$_3$-DNBP is a suitable model compound for CPF [1]. The absorption spectra of 2-DNBP and CH$_3$-DNBP and the transient absorption spectrum of CPF produced by the flash photolysis of 2-DNBP using the second harmonic of a ruby laser [2] are shown in Fig. 2.

2.2. Experiments

The experimental arrangement for the absorption saturation measurements using nanosecond light pulse excitation is shown in Fig. 3. The samples were irradiated using light pulses with the following parameters: λ = 530 nm; pulse duration, about 90 ns; pulse energy, about 30 mJ. These pulses were obtained by frequency doubling the 1.06 μm line of a Q-switched neodymium glass laser L using a lithium iodate crystal second harmonic generator SHG. The CH$_3$-DNBP and CPF samples S were contained in 5 mm sealed quartz cells degassed by repeated freeze−thaw cycles. The cells were placed in a cryostat C, the temperature of which could be stabilized within the range from 191 K to room temperature. The power transmission of the light pulses passing through the samples was measured as a function of the photon flux density $q(0)$ of the light pulse at the entrance to the quartz cells. $q(0)$ was varied using neutral filters NF. The intensities of the light pulses in front of and behind the sample were measured using two photomultipliers (PMP1 and PMP2).

CPF has a lifetime of 0.5 s at room temperature [2, 5]. Therefore the ethanolic solution of 2-DNBP was cooled to 218 K inside the cryostat and was then exposed to UV radiation (λ = 365 nm) from a mercury lamp for several minutes. The CPF produced by this process is stable for more than 1 h. The small signal transmissions T_0 of CH$_3$-DNBP and CPF were measured at 293 K and 218 K respectively using a UV−visible spectrometer.

The lifetimes of the S$_1$ states of CH$_3$-DNBP (293 K) and CPF (218 K) were measured using the picosecond probe beam spectrometer described in refs. 6 and 7. The samples were excited by the second harmonic (λ = 530 nm; pulse duration, about 10 ps; energy, 0.5 mJ pulse^{-1}) of a mode-locked neodymium glass laser. The absorption of the flashed compounds was probed using delayed pulses of second-harmonic radiation and continuous-wave ultrashort radiation. In particular we measured the repopulation time of the electronic ground states of CH$_3$-DNBP and CPF.
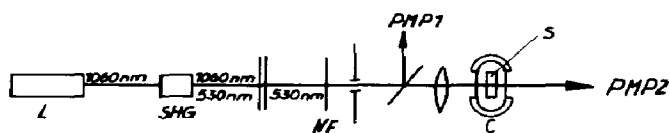

Fig. 3. Experimental arrangement for absorption saturation measurements by nanosecond light pulse excitation.

3. Results and discussion

3.1. Determination of the absorption cross section σ_0 of the coloured polymethine form at $\lambda = 530$ nm

The dependence of the power transmission T of nanosecond light pulses on the photon flux density $q(0)$ is shown in Fig. 4.

Firstly T *versus* $q(0)$ was measured for CH_3-DNBP. The absorption cross section σ_0 ($S_1 \leftarrow S_0$ transition) was determined from the absorption spectrum and the solution concentration. The curve in Fig. 4(a) was obtained by fitting the calculated transmissions (eqn. (A7)) to the experimental points. The decay constant k_{30}^{-1} of the S_1 state of CH_3-DNBP was obtained directly from picosecond probe beam measurements (Fig. 5). This approach enabled us to determine σ_3 for the $S_2 \leftarrow S_1$ transition of CH_3-DNBP and to calibrate the photon flux density scale.

σ_0 ($S_1 \leftarrow S_0$) for CPF was determined in a similar manner. We measured T as a function of the calibrated photon flux densities. The relaxation rate k_{30} of CPF was determined by picosecond probe beam absorption spectroscopy (Fig. 5). σ_0 ($S_1 \leftarrow S_0$) and σ_3 ($S_2 \leftarrow S_1$) of CPF were determined by fitting theoretical curves to the experimental points (Fig. 4(b)). The values are listed in Table 1.
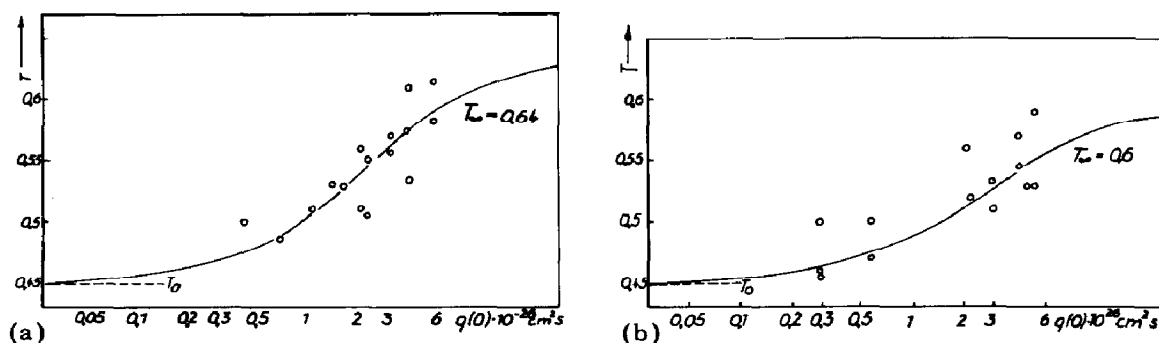

Fig. 4. Dependence of the power transmission T of nanosecond light pulses on the photon flux density $q(0)$ for (a) CH_3-DNBP (293 K) and (b) CPF (218 K).
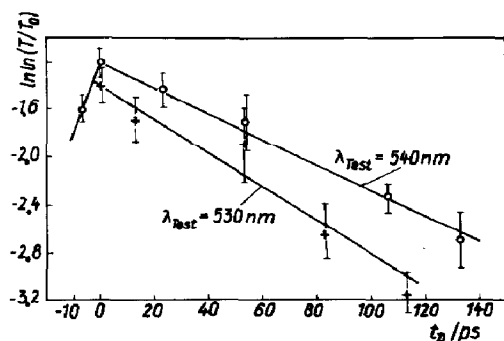

Fig. 5. Dependence of the test beam transmissions of CH_3-DNBP (293 K) and CPF (218 K) on the time after picosecond pulse excitation ($T_0 = 0.35$).

TABLE 1

Absorption cross sections σ_0 ($S_1 \leftarrow S_0$ transition at $\lambda = 530$ nm) and σ_3 ($S_2 \leftarrow S_1$ transition at $\lambda = 530$ nm) and the relaxation rate k_{30} of the S_1 state

	σ_0 (cm^2)	σ_3 (cm^2)	k_{30} (s^{-1})
CH$_3$-DNBP (293 K)	7×10^{-17}	4×10^{-17}	1.1×10^{10}
CPF (218 K)	8×10^{-17}	5.1×10^{-17}	1.4×10^{10}

3.2. Determination of the quantum yield of the photochemical reaction 2-DNBP → CPF

We have previously investigated 2-DNBP by means of nanosecond laser flash photolysis [2, 5] and picosecond probe beam spectroscopy [8]. In both experiments 2-DNBP was irradiated using the second harmonic of a ruby laser ($\lambda = 347$ nm). Transient absorptions of CPF and the aci-nitro form were measured. It was shown that there were two possible routes for the photochemical generation of CPF: a direct reaction 2-DNBP → CPF and an alternative path via an intermediate aci-nitro form. The transient spectrum of CPF [8, 9] and the experimentally determined absorption cross section $\sigma_0(\lambda = 530$ nm) of the $S_1 \leftarrow S_0$ transition of CPF can be used to determine the quantum yields of both types of reaction.

The quantum yields were determined using the following relation:

$$\ln T_\lambda = -\sigma_{0\lambda}\phi \frac{E}{Fh\nu} \{1 - \exp(-\sigma NL)\}$$

where T_λ is the transmission of the probe beam at wavelength λ, $\sigma_{0\lambda}$ is the absorption cross section of CPF at λ ($\sigma_{0\lambda}(530$ nm$) \approx \sigma_0$), E is the energy of the exciting pulses ($\lambda = 347$ nm), F is the cross section of the exciting beam at the cell entrance, $h\nu$ is the energy of the exciting photons, N is the number of 2-DNBP molecules per unit volume, σ is the absorption cross section of 2-DNBP at $\lambda = 347$ nm ($\sigma = 1.7 \times 10^{-22}$ m^2) and L is the length of the cell. This equation is a good approximation if $\phi\sigma(E/Fh\nu)$ is much less than unity (see ref. 10, Appendix A). The calculated quantum yields are listed in Table 2.

TABLE 2

Quantum yields of the direct reaction (2-DNBP → CPF) and the reaction via an intermediate (2-DNBP → aci-nitro form → CPF)

Reaction	Excitation wavelength (nm)	Quantum yield ϕ
2-DNBP → CPF	347	0.024
2-DNBP → aci-nitro form → CPF	347	0.019

Acknowledgment

The authors are grateful to D. Klemm and E. Klemm for preparing the compounds.

References

1 E. Klemm and D. Klemm, *J. Prakt. Chem.*, *321* (1979) 407.
2 D. Klemm, E. Klemm, A. Graness and J. Kleinschmidt, *Chem. Phys. Lett.*, *55* (1978) 113.
3 G. Wettermark and J. Sousa, *J. Phys. Chem.*, *67* (1963) 874.
4 D. Klemm and E. Klemm, *Z. Chem.*, *15* (1975) 47.
5 D. Klemm, E. Klemm, A. Graness and J. Kleinschmidt, *Z. Phys. Chem. (Leipzig)*, *260* (1979) 555.
6 S. Belke, *Thesis*, Friedrich Schiller University, Jena, 1980.
7 K. Vogler, *Thesis*, Friedrich Schiller University, Jena, 1980.
8 A. Graness, E. Heumann, J. Kleinschmidt, W. Triebel, D. Klemm and E. Klemm, *Adv. Mol. Relaxation Interact. Processes*, *22* (1982) 89.
9 J. Kleinschmidt, *Thesis*, Friedrich Schiller University, Jena, 1981.
10 J. Kleinschmidt and A. Graness, *J. Photochem.*, *22* (1983) 33.

Appendix A

We use the four-level system shown in Fig. A1 to calculate the intensity-dependent transmission of nanosecond light pulses.

We assume $k_{13}, k_{23} \gg k_{30}$ ($k_{13}, k_{23} \approx 10^{12} \text{ s}^{-1}$; $k_{30} \approx 10^{10} \text{ s}^{-1}$). Then the inequality $N_1, N_2 \ll N_0, N_3$ holds for the population number densities. The molecular number density will then be given by

$$N(z) = N_0(z, t) + N_3(z, t)$$

where z is the coordinate in the beam direction. The following equations are obtained for the population number densities $N_0(z, t)$ and $N_3(z, t)$ and the photon flux density $q(z, t)$:
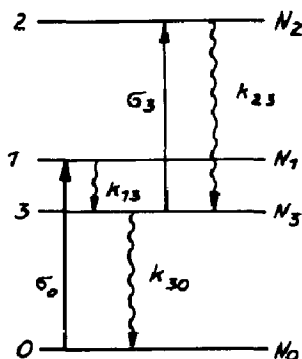

Fig. A1.

$$\frac{\partial\{N_0(z, t)\}}{\partial t} = -\sigma_0 N_0(z, t)q(z, t) + k_{30}N_3(z, t) \tag{A1}$$

$$\frac{\partial\{N_3(z, t)\}}{\partial t} = \sigma_0 N_0(z, t)q(z, t) - k_{30}N_3(z, t) \tag{A2}$$

$$N(z) = N_0(z, t) + N_3(z, t) \tag{A3}$$

$$\frac{\partial\{q(z, t)\}}{\partial z} = -\sigma_0 N_0(z, t)q(z, t) - \sigma_3 N_3(z, t)q(z, t) \tag{A4}$$

Equations (A1) - (A3) can be solved using the following assumptions: $\Delta \gg k_{30}^{-1}$ ($\Delta = 9 \times 10^{-8}$ s; $k_{30}^{-1} \approx 10^{-10}$ s) and $c\Delta \gg L$ where Δ is the pulse length, c is the velocity of light in the medium and L is the length of the cell. The following differential equation is obtained for the photon flux density $q(z, t)$:

$$\frac{\partial q(z, t)}{\partial z} = -\frac{\sigma_0 N(z)k_{30}q(z, t)}{\sigma_0 q(z, t) + k_{30}} - \frac{\sigma_3\sigma_0 N(z)q^2(z, t)}{\sigma_0 q(z, t) + k_{30}} \tag{A5}$$

After integration of eqn. (A5) we obtain

$$\left\{\frac{\sigma_3 q(L, t) + k_{30}}{\sigma_3 q(0, t) + k_{30}}\right\}^{\sigma_0/\sigma_3 - 1} \frac{q(L, t)}{q(0, t)} = \exp\left\{-\int_0^L N(z)\sigma_0\,dz\right\} \tag{A6}$$

where $q(L, t)/q(0, t)$ is the transmission T of the light pulses at time $t \leqslant \Delta$. From eqn. (A6) we obtain

$$q(0, t) = \frac{k_{30}}{\sigma_3}\frac{1 - (T_0/T)^{(\sigma_0/\sigma_3 - 1)^{-1}}}{(T_0/T)^{(\sigma_0/\sigma_3 - 1)^{-1}} - T} \tag{A7}$$

where T_0 is the small signal transmission and is given by

$$T_0 = \exp\left\{-\int_0^L N(z)\sigma_0\,dz\right\}$$

The transmission T_∞ at very high photon flux densities $q(0)$ is given by

$$\frac{\ln T_\infty}{\ln T_0} = \frac{\sigma_3}{\sigma_0} \tag{A8}$$