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Deactivation of excited xanthene dye dimers[☆]

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Abstract

Photoacoustic calorimetry was used to investigate the deactivation of electronically excited dimers of rhodamine B and eosin Y in water. Temperature dependence experiments were used to evaluate a possible photodissociative deactivation path, which should be accompanied by chemical volume changes. The quantitative evaluation demonstrates that photodissociation plays no role. Radiationless deactivation occurs for both dimers with unit quantum yield. Since the entire absorbed photon energy is released very rapidly as heat, deactivation occurs by internal conversion but not by intersystem crossing.

Keywords: Deactivation; Excited xanthene dye dimers; Photoacoustic calorimetry

1. Introduction

Many organic dye molecules dissolved in water form dimers at high concentrations, leading to changes in the low-energy absorption bands and a drastic reduction in fluorescence [1]. This effect is explained by the splitting of the lowest excited singlet state M_1 of the monomer into two excited singlet states D_1 and D_2 of the dimer [1,2]. The radiative transition from D_1 to the ground state D_0 of the dimer becomes forbidden if linear monomers, such as thionine, are aligned face-to-face in the dimer, whereas the transition $D_0 \rightarrow D_2$ becomes stronger. Rapid decay from D_2 to the non-emitting D_1 state prevents fluorescence of the dimer.

If the non-linear molecule rhodamine B (RB) associates in water, sandwich-type dimers (H aggregates) are formed [3,4]. The state splitting is still preserved, whereas, because of the reduced molecular symmetry, the radiative selection rules are weakened [1,2,5]. Therefore the first absorption band of the RB monomer ($\lambda_{max} = 554$ nm) is split into two bands ($\lambda_{max} = 526$, 560 nm) of comparable strength for the dimer [5]. Nevertheless, practically no dimer fluorescence is observed in water [4,5]. The almost complete radiationless deactivation of the excited dimer occurs on a very fast time scale. Time-resolved absorption experiments have revealed that the ground state of the RB dimer is repopulated with a time constant of 100 ps [6]. Since the excitation energies of D_1 and M_1 are of similar magnitude, internal conversion (IC) from both excited species could be expected to proceed with a similar rate. However, the lifetime of 1.6 ns of M_1 [6,7] is distinctly longer than the lifetime of D_1. M_1 is deactivated by fluorescence emission with a rate constant $k_F = 1.9 \times 10^8$ s^{-1} [7]. Radiationless deactivation occurs with $k_{IC} = 4.2 \times 10^8$ s^{-1} [7] since, for M_1, intersystem crossing (ISC) is about two orders of magnitude slower than IC [8]. The probability that ISC contributes significantly to the non-radiative decay of D_1 during the short lifetime of 100 ps is rather low. Indeed, as demonstrated below, ISC can be ruled out on the basis of the results of time-resolved photoacoustic calorimetry (PAC) measurements. However, a different process could be responsible for the fast radiationless deactivation of D_1. The photodissociation of D_1 into two ground state monomers M_0 according to Eq. (1) has been discussed as a possible fast deactivation process of D_1 [4,6].

$$D_1 \xrightarrow{\Delta V_R} 2M_0 \tag{1}$$

$$2M_0 \xrightarrow{-\Delta V_R} D_0 \tag{2}$$

Photodissociation (1) should be distinguished by a positive reaction volume ΔV_R. Suzuki and Tsuchiya [9] determined, in pressure-dependent absorption measurements, that the reaction volume for the dimerization reaction (Eq. (2)) is -10.4 ml mol^{-1}. Therefore $\Delta V_R = 10.4$ ml mol^{-1} is expected for photodissociation

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[☆] Dedicated to Professor H.-D. Brauer on the occasion of his 60th birthday.

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(1) assuming that the partial molar volumes of the ground and excited state dimers are the same. The back reaction (Eq. (2)) of the RB monomers occurs in the millisecond time domain [10]. Therefore PAC, which can be used for the determination of photochemically induced molecular volume changes if products have lifetimes of at least 10^{-5} s [11–13], should be appropriate to investigate whether process (1) is an effective deactivation path of the excited RB dimer.

PAC measures the pressure wave which develops in a sample volume illuminated by a short laser pulse. Thermal expansion $\Delta v_{th}(T)$, caused by the release of heat during radiationless deactivation, and chemically induced volume changes Δv_r contribute to the overall fast volume change $\Delta v(T)$ [12]

$$\Delta v(T)=\Delta v_{th}(T)+\Delta v_r \qquad (3)$$

$\Delta v_{th}(T)$ is proportional to the thermal expansion coefficient $\beta(T)$ of the solution. Because of the anomalous temperature dependence of the density of water, temperature-dependent measurements of photoacoustic waves can yield quantitative information about photochemically induced volume changes [11–13]. We used this method to investigate the radiationless deactivation of electronically excited dimers of RB and eosin Y (EO) [5].

2. Experimental details

The photoacoustic cell used front face illumination and has been described previously [14]. It is a copy of the instrument developed by Melton et al. [15]. Excitation pulses were provided by an excimer laser (EMG 200E) pumped dye laser (Fl 3002), both from Lambda Physik, Göttingen. The pulse width was 25 ns. Sample and reference solutions had the same optical density at the excitation wavelength. The solutions were stored in reservoirs, where they were deoxygenated by a stream of Ar gas saturated with water vapour. Sample and reference solutions passed alternately through the PAC cell (optical path length, 0.026 cm). The whole cell, including the 1 MHz transducer (A103S, Panametrics, Hofheim), was placed into a PVC housing equipped with a window made of an evacuated quartz cuvette. The connection to the transducer was sealed by water-insoluble elastic adhesive. The housing was then filled with distilled water circulating in a thermostat. In this way, PAC experiments could be performed at various temperatures T. Photoacoustic waves were averaged over 100 laser shots. For each measurement, the laser pulse energy dependence was examined. Only linear energy results were employed. The evaluation followed literature procedures [15]. Monoexponential heat evolution functions with a time constant $\tau_S=1$ ns were required in the convolution procedure. Therefore the radiationless decays were detected integrally with an integration time of 50 ns or less. Thus the amplitudes of the acoustic waves are proportional to the volume changes in the fast deactivation. Slow processes with time constants of 20 μs or more were not detected because of the vanishing amplitudes. RB, EO (both from Merck) and bromocresol purple (BCP) were used as supplied.

3. Results and discussion

3.1. General procedure of evaluation

The amplitudes $A_D(T)$ and $A_R(T)$ of the transducer signals of the dimeric species and photoacoustic reference respectively are directly proportional to the laser-induced volume changes. The reference compound BCP releases the entire absorbed photon energy as prompt heat, $A_R(T)\propto\Delta v_{th,R}(T)$ [11], whereas the photoacoustic signal related to the dimers may have thermal and photochemical contributions, $A_D(T)\propto(\Delta v_{th,D}(T)+\Delta v_{r,D})$. If dimer and reference are excited using identical conditions, the ratio $\alpha_D(T)$ of the amplitudes is given by

$$\alpha_D(T)=\frac{A_D(T)}{A_R(T)}=\frac{\Delta v_{th,D}(T)}{\Delta v_{th,R}(T)}+\frac{\Delta v_{r,D}}{\Delta v_{th,R}(T)} \qquad (4)$$

It is assumed that $\Delta v_{r,D}$ is constant in the temperature range investigated (298–277 K). In this case, the thermal and photochemical volume effects can be separated by temperature-dependent measurements of $\alpha_D(T)$ [12,13]. With the reference temperature 298 K, we define $X(T)=\Delta v_{th,R}(298)/\Delta v_{th,R}(T)$ and $\alpha_{r,D}(298)=\Delta v_{r,D}/\Delta v_{th,R}(298)$ and obtain

$$\alpha_D(T)=\alpha_{th,D}+\alpha_{r,D}(298)X(T) \qquad (5)$$

where $\alpha_{th,D}$ is the temperature-independent fraction of the absorbed photon energy, which is released by the dimer on a time scale faster than the heat integration time of about 50 ns. A plot of $\alpha_D(T)$ against $X(T)$ should be linear and result in an intercept $\alpha_{th,D}(T)$ and slope $\alpha_{r,D}(298)$. The slope is related directly to the molar reaction volume ΔV_R of a photoreaction with quantum yield Q_R [12,13].

$$Q_R\Delta V_R=\alpha_{r,D}(298)E_L\beta(298)/(c_P\rho) \qquad (6)$$

where E_L is the molar energy of the exciting laser photons, $\beta(298)=2.57\times10^{-4}$ K^{-1} [16], $c_P=4.19$ J K^{-1} g^{-1} and $\rho=1.00$ g ml^{-1}.

3.2. Deactivation of the excited RB dimer

Fig. 1 displays the photoacoustic waves measured with a concentrated solution of RB in water at different

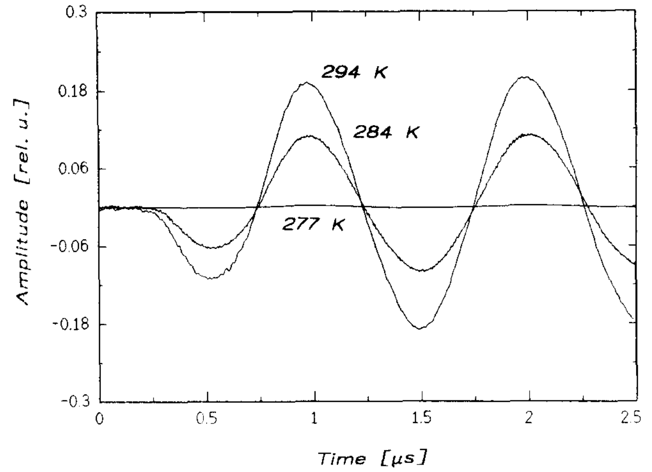

Fig. 1. Photoacoustic waves recorded with RB in H_2O at different temperatures. $[RB]=2.42\times10^{-3}$ M, referred to monomers.

Table 1
Parameters of temperature-dependent photoacoustic experiments with RB in H_2O

T (K)	298	294	284	281
K (M^{-1})	1500	1720	2464	2758
$[M_0]$ (10^{-4} M)	7.47	7.06	6.07	5.78
$[D_0]$ (10^{-4} M)	8.37	8.57	9.07	9.21
$f_M(T)$	0.214	0.200	0.169	0.160
$f_D(T)$	0.786	0.800	0.831	0.840
$Q_F(T)$	0.30[a]	0.32_8	0.40_8	0.43_4
F_{RA}	0.56	0.56_3	0.56_6	0.56_7
$\alpha_M(T)$	0.907	0.897	0.872	0.863
$\alpha_S(T)$	0.994	0.996	0.994	1.056
$\alpha_D(T)$	1.018	1.021	1.019	1.093
$X(T)$	1.00	1.66	2.79	4.21

[a] Literature value: 0.31 [8].

temperatures. A strong dependence of the amplitude $A_S(T)$ of the sample on the temperature is revealed. Before starting the quantitative evaluation, it is necessary to consider that, at the concentration employed, both dimers and monomers are excited. With $f_M(T)$ and $f_D(T)$ being the fractions of laser light absorbed by the monomers and dimers respectively, we obtain

$$\alpha_D(T)=[\alpha_S(T)-f_M(T)\alpha_M(T)]/f_D(T) \qquad (7)$$

where $\alpha_M(T)$ is the portion of absorbed photon energy released by the monomer as prompt heat and $\alpha_S(T)=A_S(T)/A_R(T)$.

The dimerization equilibrium constant $K=[D_0]/[M_0]^2$ was determined for RB to be $K=1500$ M^{-1} at 298 K [5]. With the dimerization enthalpy of -25 kJ mol^{-1} [3], we derive values of K at the temperatures of the PAC experiments (Table 1). Using the concentration of RB of 2.42×10^{-3} M, calculated as if only monomers were present in the solution, we obtain the equilibrium concentrations $[D_0]$ and $[M_0]$ listed in Table 1. The absorption spectra of the monomer and dimer of RB were determined by Förster and König [5]. Taking the extinction coefficients at the laser wavelength of 520 nm ($E_L=230$ kJ mol^{-1}) ($\epsilon_M=35\,000$ M^{-1} cm^{-1} and $\epsilon_D=115\,000$ M^{-1} cm^{-1}), we calculate the values of $f_M(T)$ and $f_D(T)$ given in Table 1. Since the only process competing with radiationless deactivation of the excited monomer is fluorescence, occurring with a quantum yield $Q_F(T)$, we calculate $\alpha_M(T)$ using

$$\alpha_M(T)=[E_L-F_{RA}Q_F(T)E_F]/E_L \qquad (8)$$

where E_F is the average fluorescence photon energy of RB and F_{RA} is the factor accounting for the reduction in emission due to reabsorption in the photoacoustic cell. F_{RA} was estimated by considering monomers and dimers as pure filters for the emitted fluorescence. For each fluorescence wavelength, the extent of absorption by monomers and dimers was calculated by averaging over all directions of space from the centre of the photoacoustic cell and hence over all possible optical path lengths. Re-emission by secondary excited monomers was neglected. Using this procedure we obtained the effective fluorescence spectrum C which is compared in Fig. 2 with the true fluorescence spectrum B of RB. The ratio of the integrated spectra yields F_{RA}. From the centre of gravity wavelength of the fluorescence spectrum C, we calculate $E_F=198$ kJ mol^{-1}. Using Eqs. (8) and (7) we finally obtain $\alpha_D(T)$, which is plotted in Fig. 3 against $X(T)$. A weighted linear least-squares fit yields $\alpha_{th,D}=1.00\pm0.04$ and $\alpha_{r,D}(298)=0.01\pm0.02$.

In agreement with the results of concentration-dependent investigations of fluorescence, it is found by temperature-dependent PAC measurements that dimers of RB are deactivated completely by radiationless processes. Deactivation occurs on the time scale of 50 ns or less, which is too fast to be consecutive ISC from

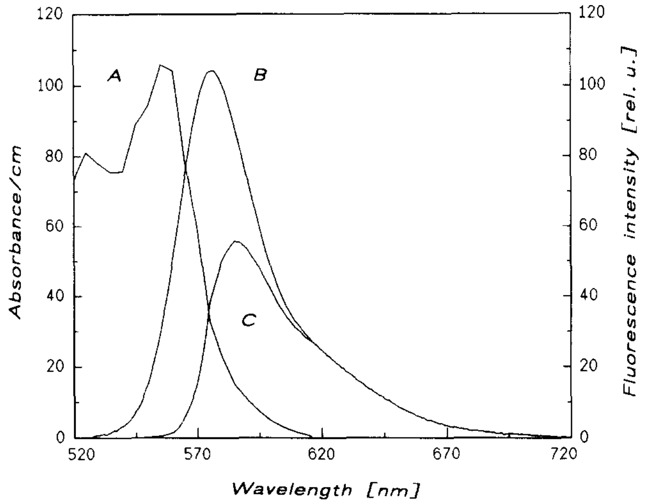

Fig. 2. (A) Absorption spectrum of $[RB]=2.42\times10^{-3}$ M calculated from the absorption spectra of monomer and dimer [5]. Corrected fluorescence spectra of RB in H_2O: (B) dilute solution; (C) concentrated solution, $[RB]=2.42\times10^{-3}$ M, calculated using spectrum A.

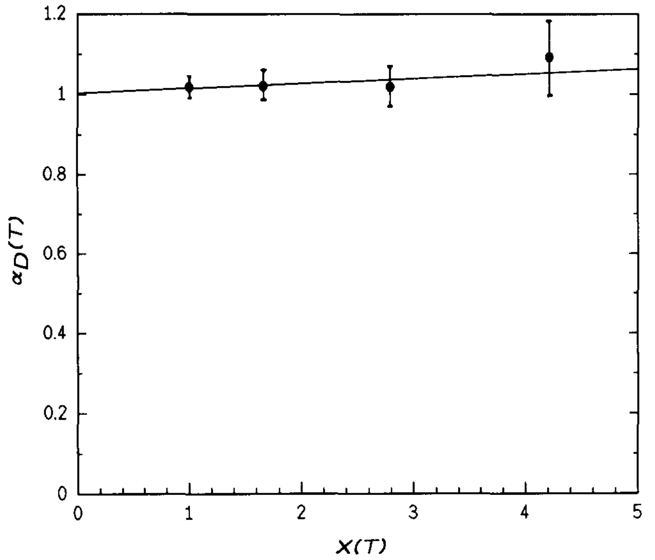

Fig. 3. Plot of $\alpha_D(T)$ vs. $X(T)$ for RB in H_2O. $[RB] = 2.42 \times 10^{-3}$ M. Straight line results from a weighted linear least-squares fit according to Eq. (5). $\alpha_{th,D} = 1.00 \pm 0.04$, $\alpha_{r,D}(298) = 0.01 \pm 0.02$.

Table 2
Parameters of temperature-dependent photoacoustic experiments with EO in H_2O; $\alpha_D(T) = \alpha_S(T)$

$\alpha_D(T)$	0.984	0.977	0.966	0.900	0.997
$X(T)$	1.00	1.32	1.76	2.16	2.92

D_1 to the lowest triplet state to D_0. Therefore ISC plays no important role in the deactivation of D_1. From Eq. (6) and $\alpha_{r,D}(298)$ we obtain for the dimer dissociation $Q_R\Delta V_R = 0.14 \pm 0.28$ ml mol^{-1}. Combination of this value with $\Delta V_R = 10.4$ ml mol^{-1}, determined by Suzuki and Tsuchiya [9] for the dissociation of ground state dimers, yields $Q_R = 0.01 \pm 0.03$. Thus photodissociation of RB dimers does not take place.

The result $Q_R \approx 0$ is in accordance with conclusions which can be drawn if the reaction enthalpy $\Delta H_R = 25$ kJ mol^{-1} of RB dimer dissociation is considered. If photodissociation occurs, Eq. (9) holds for the prompt heat released by the dimer, since the back reaction (Eq. (2)) of monomers is too slow to be detected by PAC

$$\alpha_{th,D} = (E_L - Q_R\Delta H_R)/E_L \qquad (9)$$

From the values given above, $Q_R\Delta H_R = 0 \pm 9$ kJ mol^{-1} results, which is compatible with $Q_R \approx 0$. Therefore we conclude that the fast (100 ps [6]) and complete radiationless deactivation of excited RB dimers occurs not by photodissociation but only by IC.

3.3. Deactivation of the excited EO dimer

The dimerization constant of EO is $K = 400$ M^{-1} [5]. Since the respective reaction enthalpy is not known, the concentration of EO was chosen to be very high to shift the equilibrium practically completely to the dimeric species. Variations of temperature can then have only a slight effect on the equilibrium concentration $[D_0]$. At 298 K, the equilibrium concentrations were $[D_0] = 0.238$ M and $[M_0] = 0.024$ M. At the excitation wavelength of 550 nm, the extinction coefficients are $\epsilon_D = 15\,000$ M^{-1} cm^{-1} and $\epsilon_M = 3500$ M^{-1} cm^{-1}. The fractions of laser light absorbed by the dimers and monomers were $f_D = 0.977$ and $f_M = 0.023$ respectively. Thus the inner filter effect by monomer absorption can be neglected and the experimental value of $\alpha_S(T)$ can be set in good approximation equal to $\alpha_D(T)$. Table 2 collects the values of $\alpha_D(T)$ and $X(T)$ determined with EO in 0.1 N NaOH with BCP as reference. The BCP solution was buffered to pH 12 to keep the indicator in its basic form. The weighted linear least-squares fit according to Eq. (5) yields $\alpha_{th,D} = 1.00 \pm 0.03$ and $\alpha_{r,D}(298) = -0.02 \pm 0.04$. These data are very similar to the results found for the RB dimer and point to the absence of a photodissociative route for the deactivation of the excited EO dimer. The value of $\alpha_{th,D}$ is in agreement with complete deactivation by IC since the heat is released during the integration time of 50 ns or less. With $E_L = 218$ kJ mol^{-1}, $\alpha_{r,D}(298)$ and Eq. (6), $Q_R\Delta V_R = -0.3 \pm 0.5$ ml mol^{-1} is obtained. Unfortunately, the ΔV_R value of the dissociation of EO ground state dimers is not known. However, presumably the reaction volume is at least as large as found for the dimers of RB and methylene blue (MB), for which $\Delta V_R = 10.6$ ml mol^{-1} was determined [9]. The reaction volume is composed additively of an intrinsic part ΔV_i, corresponding to structural volume changes of the reacting molecules, and a solvation part ΔV_S, resulting from changes in the electrostriction around the reacting species. It can be assumed that ΔV_i has approximately the same value for the dissociation of RB, MB and EO dimers. However, ΔV_S differs. Dissociation of a twofold charged ion into two singly charged ions (RB, MB) is accompanied by a positive ΔV_S value, since the electrostriction volume correlates with the square of the electric charge of the dissolved species according to the Drude–Nernst equation [17,18]. Since the dimer of EO carries four negative charges, a larger positive ΔV_S value and, consequently, ΔV_R is expected for this dye. Therefore $Q_R = 0$ results within an uncertainty of about 0.02. Thus EO photodissociation does not take place.

4. Conclusions

The dimers of the xanthene compounds RB and EO have been taken as models for the investigation of the radiationless deactivation of non-fluorescent face-to-face aggregates in water. The results of temperature-dependent PAC experiments clearly reveal that deactivation of the excited dimers occurs quantitatively by fast IC. No evidence for a photodissociative deactivation path or for ISC has been found.

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