

Luminescence Quenching of Rhodamines by Cyclooctatetraene

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Z. Naturforsch. **42a**, 1009–1013 (1987); received June 24, 1987

Cyclooctatetraene (COT) as a quencher of fluorescence of a series of Rhodamine solutions was studied. The second order rate constants for the quenching process of Rhodamine 110, Rhodamine 19 pchl., Rhodamine 6G pchl., Rhodamine 6G, Tetramethylrhodamine, Rhodamine B and Rhodamine 3B pchl. are given. It was found that COT enhances rather intersystem crossing than internal conversion.

Key words: Quenching of Fluorescence, Rhodamines, Cyclooctatetraene

Introduction

The efficiency of laser generation of flashlamp pumped dye lasers depends considerably on the population of the first excited triplet state and on the triplet–triplet absorption [1]. A marked improvement of laser performance of a dye laser can be achieved when a triplet quencher is added to the dye solution being an active medium. Some inorganic as well as organic triplet quenchers are known [2, 3]. As a triplet quencher for xanthene dyes very often 1,3,5,7-cyclooctatetraene- C_8H_8 (COT) is used. For the quenching of the Rh6G triplet state by COT the rate constant is given by Dempster [4] to be $(7.0 \pm 0.1) \cdot 10^8 M^{-1} s^{-1}$ assuming a diffusion controlled process. On the other hand Rubinov *et al.* [5] claim that the triplet lifetime of Rh6G in ethanol increases in the presence of COT. In this case the improvement of laser performance of flash-pumped dye lasers caused by COT addition is explained by the simultaneous decrease of the yield of triplet formation. It was also suggested that COT quenches the fluorescence of Rhodamine solutions [6], but the mechanism whereby COT increases the overall radiationless decay rate of singlet states of dye molecules has not yet been established. In other words, the effect of COT on dye molecules can not be considered as fully understood. In this paper, results of investigations on COT as a singlet quencher are presented.

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Experimental

Ethanol solutions of various Rhodamines where investigated; the maxima of their absorption and emission spectra, the fluorescence decay times, quantum yields, total nonradiative transition rates, and the energy of 0–0 transitions are given in Table 1. Corrected fluorescence spectra are shown in Figure 1. The difference in excited singlet energies are due to the different substituents attached to the dye molecule moiety.

The quantum yield has been determined by the Parker-Rees method [7] using Rh6G in EtOH (quantum yield 0.88, as obtained by Olmsted by means of a calorimetric method [8]) as a standard. Specifically, the corrected fluorescence spectrum of the reference sample and then the unknown spectrum were measured. Relative excitation fluxes were controlled by means of a photomultiplier with a photon counter (Rh B in glycol ethylene, $c = 8 g/l$ [9]).

The fluorescence yield of Rhodamine molecules in solution may be suppressed by perturbations of substituents or by external influences. The rate

Table 1. Spectroscopic properties of Rhodamines in EtOH solutions.

Rhodamine	E_{0-0} (eV)	λ_{abs}^{max} (nm)	λ_{fl}^{max} (nm)	τ_0 (ns)	ϕ_{fl}	k_{NR}^0 ($10^7 s^{-1}$)
Rh 110	2.41	505	524	4.2	0.99	0.24
Rh 19 pchl	2.33	521	547	4.4	0.94	1.45
Rh 6G pchl	2.28	530	554	4.45	0.86	3.1
Rh 6G	2.28	530	555	4.4	0.88	2.7
TmRh pchl	2.24	543	568	3.4	0.60	11.8
Rh B	2.22	548	572	3.2	0.59	12.8
Rh 3B pchl	2.18	555	581	2.4	0.39	25.6

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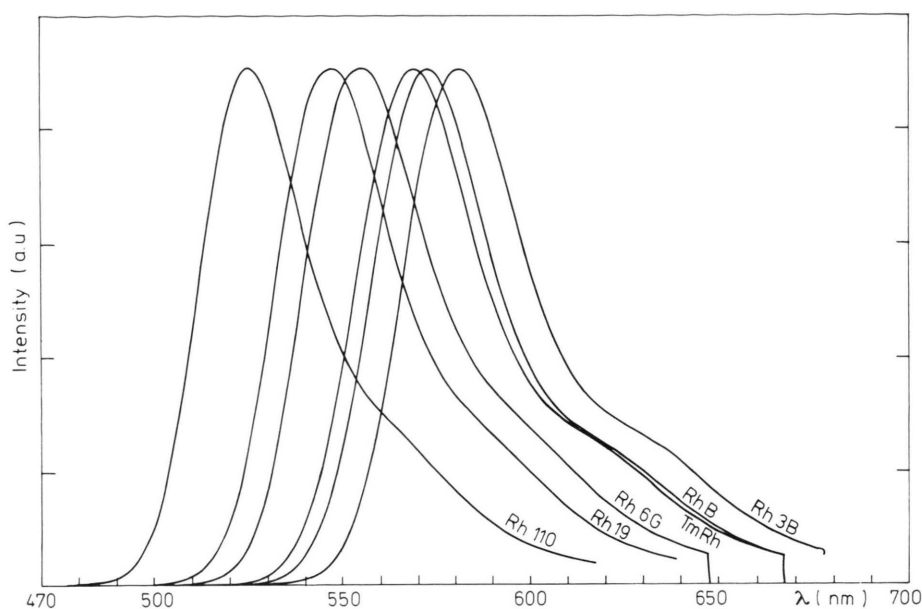


Fig. 1. Normalized fluorescence spectra of Rhodamines in EtOH (corrected). The abbreviations correspond to Eastman Kodak notation.

constants for fluorescence quenching of Rhodamines in ethanol by COT were determined from a Stern-Volmer treatment of the fluorescence yield data using a two-beam fluorimeter described elsewhere [10]. The quenching constants K and rate parameters k_q (calculated from K and τ_0) are listed in Table 2.

Laser grade Rhodamines from Estman Kodak and analytically pure ethanol from POCH-Gliwice were used without further purification. Cyclooctatetraene from Merck (for synthesis) was used after a filtering procedure. The concentration of dye molecules in solution was always 10^{-5} M, and a suitable dose of stock solution (of 1 M COT in 10^{-5} M of dye solution) could be automatically added to a measuring vessel with the dye solution. The measuring vessel was not removed throughout the whole measuring cycle. It is believed that chemi-

cal reactions between solute and disturber molecules, when present, do not introduce significant additional effects during the time interval between the preparation of the samples and their measurement. Also photoinduced processes, because of the low excitation intensity conditions in the applied experimental procedure, do not have to be taken into account.

Results and Discussion

In all investigated Rhodamine solutions the fluorescence intensity decreases according to the Stern-Volmer equation

$$I_0/I = 1 + K[Q], \quad (1)$$

where K and $[Q]$ are the quenching constant and the concentration of COT, respectively, see Fig. 2 and Table 2. For simplicity experimental points are indicated for Rh 6G only. No changes in the solution absorption spectrum with increase in COT concentration are observed, which allows to admit that

$$I_0/I = \phi_0/\phi, \quad (2)$$

ϕ and ϕ_0 being the quantum yields of fluorescence in the presence and the absence of quencher, respectively.

Table 2. Fluorescence quenching rates of Rhodamines by COT.

Rhodamine	K (M^{-1})	k_q ($10^9 M^{-1} s^{-1}$)
Rh 110	2.17 ± 0.03	0.52
Rh 19 pchl	0.39 ± 0.01	0.09
Rh 6G pchl	0.674 ± 0.005	0.15
Rh 6G	0.740 ± 0.005	0.17
TmRh pchl	0.42 ± 0.01	0.125
Rh B	0.22 ± 0.01	0.07
Rh 3B pchl	0.05 ± 0.01	0.02

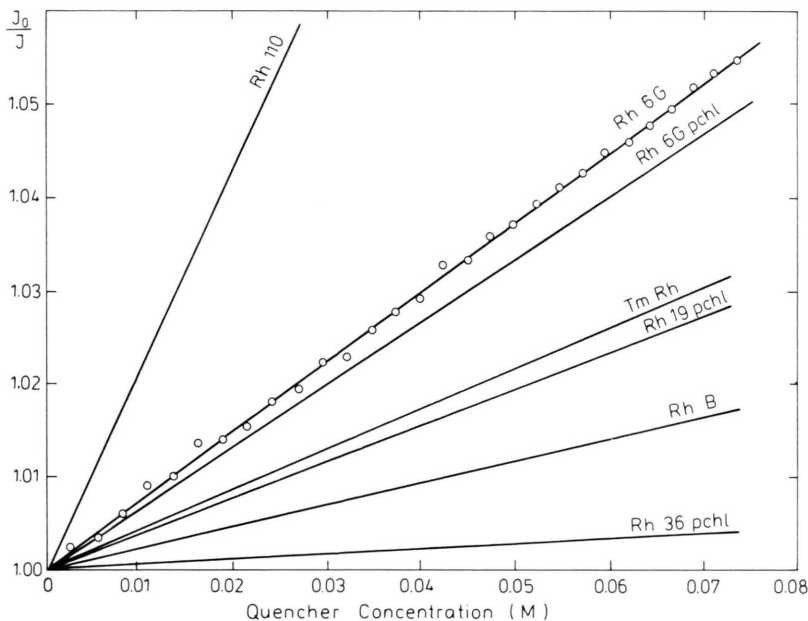


Fig. 2. Stern-Volmer plots for the quenching of Rhodamines by COT. Fitted lines to experimental data are presented. For better legibility experimental points are depicted only for Rh6G.

Direct fluorescence lifetime measurements reveal an equivalent decrease in the fluorescence efficiency and lifetime [11]; hence a collisional quenching mechanism can be assumed. In this case the Stern-Volmer equation reads

$$\begin{aligned} \phi_0/\phi &= (k_R + k_{NR}^0 + k_q[Q]) / (k_R + k_{NR}^0) \\ &= 1 + \tau_0 k_q [Q], \end{aligned} \tag{3}$$

where $\tau_0^{-1} = k_R + k_{NR}^0$ is the decay rate of the fluorescence in the absence of quencher, k_q is the bimolecular quenching rate constant, k_R and k_{NR}^0 being the radiative and radiationless transition rate constants, respectively. Thus the increase of the rate of the radiationless transition can be treated as the result of the quencher action:

$$k_{NR} = k_{NR}^0 + k_q [Q], \tag{4}$$

where $k_{NR}^0 = k_{IC}^0 + k_{ISC}^0$.

The internal quenching rate k_{NR}^0 in the absence of COT, as determined by

$$k_{NR}^0 = (1 + \phi_0) / \tau_0 \tag{5}$$

is listed in Table 1.

With regard to the position of the first absorption band of COT, centered at 280 nm, an energy transfer from excited dye molecules to COT can be excluded. This leads to the assumption that COT causes a perturbation of the intramolecular elec-

tronic relaxation rates in the excited dye molecules. Therefore the relation (4) can be expressed in the form

$$k_{NR} = k_{IC} + k_{ISC}, \quad \text{where} \tag{6}$$

$$k_{IC} = k_{IC}^0 + k_{q,IC}[Q] \quad \text{and} \tag{7a}$$

$$k_{ISC} = k_{ISC}^0 + k_{q,ISC}[Q] \quad \text{with} \tag{7b}$$

$$k_{q,IC} + k_{q,ISC} = k_q. \tag{7c}$$

It has to be emphasised that the typical Stern-Volmer treatment of the fluorescence yield reveals only the total quenching constant k_q . To find out which of the processes in (7) are activated by COT, a discussion is performed basing on the behaviour of the whole series of Rhodamines.

The values of the radiationless transition rates given in (4) were obtained experimentally for the investigated series of Rhodamines (Figure 3). Their logarithms are plotted against the energy gap ΔE between the zero point vibrational levels of the first excited singlet and the ground state and appear to follow a linear dependence on this energy gap; thus the energy gap law [12] for the series of Rhodamines is fulfilled (Fig. 3, curve a). The second order rate constant given in (4) reveals a quite different energy gap dependence (Fig. 3, curve b).

The value of $k_{ISC}^0 \leq 10^6 \text{ s}^{-1}$ was announced for several Rhodamines [13, 14, 15], the values of k_{NR}^0

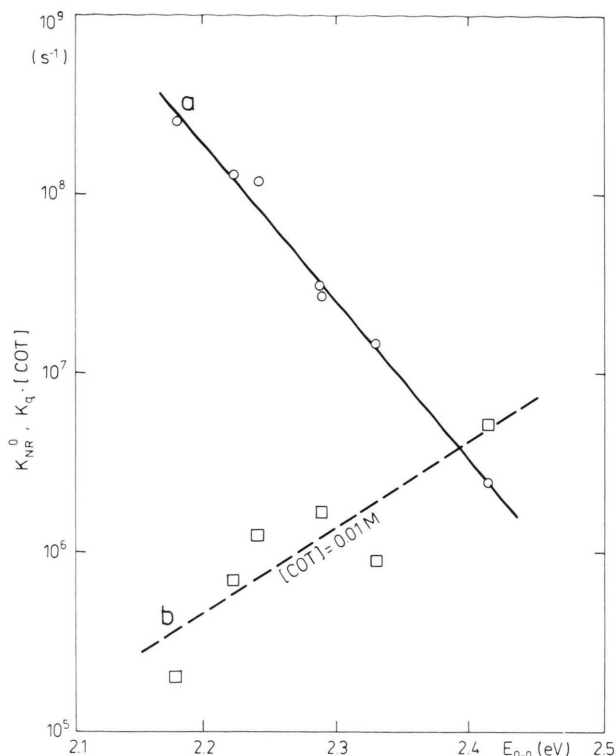


Fig. 3. Radiationless transition rates of Rhoadmines versus energy of 0-0 transition. a) Internal quenching rate k_{NR}^0 without COT, b) COT quenching rate $k_q[COT]$, ($[COT] = 0.01 M$).

listed in Table 1 range from $2.4 \cdot 10^6 s^{-1}$ to $2.5 \cdot 10^6 s^{-1}$ and are (except Rh 110) an order or two larger than k_{ISC}^0 . This means that the internal quenching k_{NR}^0 is almost equal to the internal conversion k_{IC}^0 and it is not surprising that the energy gap law is fulfilled. If we put $k_{IC} \approx \exp(-\alpha \Delta E)$, where the energy gap ΔE is obtained from intersection of absorption and emission spectra taken in proper units, then from our data we get $\alpha = 8.8 eV^{-1}$.

The quenching process by COT, illustrated for a fixed COT concentration in Figure 3, depends on

the energy of the excited singlet state of Rhodamines. If the perturbation caused by COT would favour the internal conversion pathway of deactivation of the singlet state, the addition of COT would increase the negative slope of *curve a* in Figure 3. The different behaviour of the whole series of Rhodamines when COT is added indicates that rather $k_{q,ISC}[Q]$ than $k_{q,IC}[Q]$ is responsible for the quenching of excited singlet states of Rhodamines.

In spite of the ascertainment that the quenching process of Rhodamines by COT is a bimolecular one, the nature of this interaction has not been deciphered. From the obtained results the conclusion can be drawn that of the two radiationless pathways from the excited singlet state chiefly the intersystem crossing is enhanced by COT. This means that a new mechanism has to be found to account for the positive action of COT on laser performance despite the increase of the intersystem crossing rate in the dye solution.

Summary

The Stern-Volmer quenching rate constants were obtained for several COT-Rhodamine dye solutions. Basing on the behaviour of a series of Rhodamines in solution with COT and on the energy gap law for Rhodamines it was possible to establish that COT causes the enhancement of the intersystem crossing rate rather than the increase of internal conversion. It has to be admitted, however, that the perturbation mechanism in Rhodamine-COT solutions is still an open question.

Acknowledgement

This work was carried out under the Polish Central Program for Fundamental Research CPBP 01.06.

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