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Photochemistry of Rhodamine 610

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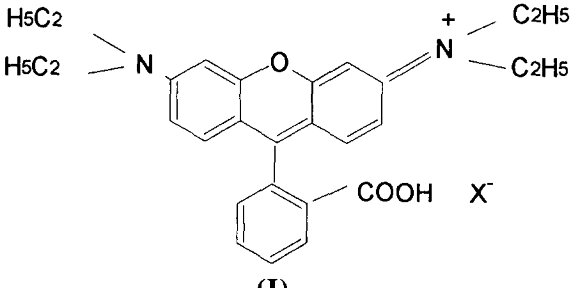
ABSTRACT

Rhodamine 610 was irradiated with a laser emitting a 511 nm. The photodegradation of this dye is very slow (quantum yield = 10^{-6}). Photochemical reactions were made in ethanol with rhodamine 610 alone, and with additives which quench the single state, the triplet state and radicals. *© 1997 Elsevier Science Ltd*

Keywords: Rhodamine 610, photodegradation, laser, formulation.

INTRODUCTION

The photochemistry of rhodamine has been actively studied because of the use of such dyes in lasers [1]. In a previous paper, the results on the photodegradation of rhodamine 640 [2] were reported, and we now present data pertaining to the spectroscopic and photochemical properties of the rhodamine 610 (I).



(I)

The main problem when using rhodamines in lasers is the photodegradation of these compounds in ethanolic solution [3], and the objective of the present experiments is to find additives which can stop this degradation. In this perspective, we have tested the influence of some compounds on the fluorescence and on the degradation of rhodamine B.

EXPERIMENTAL

The irradiation source was a copper vapour laser which emitted at 511 nm. The impulse energy was 1,4 mJ with a period of 50 ns; the frequency was 6.5 kHz and the volume of the reaction cell 12.5 ml.

Fluorescence spectra were recorded on a Kontron model SFM 25 fluorimeter and absorption spectra were recorded on a Perkin Elmer Lambda 5 and a Kontron Uvikon 930.

The photodegradation of rhodamine was carried out in ethanol, and its concentration was measured by HPLC with a DIOL reverse phase column. The solvent used was a mixture of methanol-water (60/40) with 1/1000 sodium hexane-sulfonate. The rhodamine concentration was 2.1 10^{-4} M. The additives which were used to decrease the degradation of the rhodamine were: DABCO, 2,6-d-tert-butyl-4-methylphenol and azulene.

RESULTS AND DISCUSSION

Spectrocopy

The fluorescence study of rhodamine 610 was performed over the concentration range of 10^{-6} M to 2.1 10^{-4} M; maximum fluorescence was obtained at 1.5 10^{-5} M. Nevertheless, we tested the selected additives at two concentrations, viz., 10^{-5} M and 2.1 10^{-4} M, and this latter concentration was used in the laser line.

The absorption maximum was 553 nm in ethanol, with an extinction coefficient $\varepsilon = 1.07\ 10^5\ M^{-1}cm^{-1}$. The fluorescence maximum was at 580 nm with a quantum yield $\phi_f = 0.71$ in ethanol.

When the rhodamine concentration was 2.10^{-4} M, the influence of additives was negligible except with azulene (Table 1). The effect of KOH and DABCO can be explained by the pH variation of the solution [4] and by dissociation of the rhodamine. The effect of azulene is dependent on the energy transfer which can exist between the singlet states of the dye and of the additive [5]:

TABLE 1
Fluorescence intensity for rhodamine 610 at concentration of 10^{-5} M, and with additives

Additives	*KCl*	*KBr*	*KOH*	*DABCO*	*Azulene*
flourescence intensity	unchanged	unchanged	with ($C = 10^{-4}$M) $\times 1.5$	with ($C = 10^{-4}$M) $\times 1.5$	decrease, which depends on the concentration

energy level of the azulene singlet state: 710 kJ mol^{-1}
energy level of the rhodamine singlet state: 890 kJ [6] mol^{-1}

Two series of experiments were performed with azulene at different concentrations of rhodamine, viz.,

a) [rhodamine] = 10^{-5} M

In these conditions the influence of azulene is low. The fluorescence intensity is reduced by a factor of two with an azulene concentration which is 200 times higher than the rhodamine concentration.

b) [rhodamine] = 2.1 10^{-4} M

In this case, the effect of azulene is important since the fluorescence intensity is reduced by 30 for an azulene concentration which is twice that of the rhodamine concentration (Fig. 1).

Kinetic

We have shown that azulene is a fluorescence quencher, and it was therefore of interest to study its influence on the photodegradation rate. Two series of experiments were carried out, using the previous rhodamine concentrations (Fig. 1). The results obtained are shown in (Table 2)

If the variations of the azulene concentrations have an important role on the rhodamine fluorescence, this role is much weaker for the photodegradation. We noted in all our experiments a decrease of the photodegradation quantum yield of the dye when azulene was added to the solution (Fig. 2), but the effect was not comparable to that obtained on the fluorescence quantum yield.

Azulene can interact with the singlet and the triplet states of rhodamine 610 as quencher of these two excited states. When we consider its action on the singlet state, we can notice a good efficiency with a rhodamine concentration higher than 10^{-4} M, and a poor efficiency with a concentration lower than this.

At 10^{-4} mol.l^{-1} concentration, the possibility of dimerisation has been reported [7, 8] and hence azulene will be more efficient on this structure than on the monomer.

We also know that the fluorescence is low at the 10^{-4}M concentration, and in these conditions the quantity of azulene will be sufficient to inhibit light

TABLE 2
Influence of azulene concentration on the rhodamine photodegradation quantum yield

[rhodamine] mol.l^{-1}	3.7 10^{-5}	6.2 10^{-5}	14.0 10^{-5}	21.0 10^{-5}	42.0 10^{-5}
[azulene] mol.l^{-1}	0	0	0	0	0
ϕD	2.3 10^{-6}	3.4 10^{-6}	6.5 10^{-6}	6.0 10^{-6}	14.0 10^{-6}
[rhodamine] mol.l^{-1}	5.0 10^{-5}	2.1 10^{-4}	5.0 10^{-4}	5.0 10^{-4}	
[azulene] mol.l^{-1}	10^{-3}	4.2 10^{-3}	10.0 10^{-3}	5.0 10^{-3}	
ϕD	4.4 10^{-7}	3.6 10^{-7}	2.5 10^{-7}	4.9 10^{-7}	

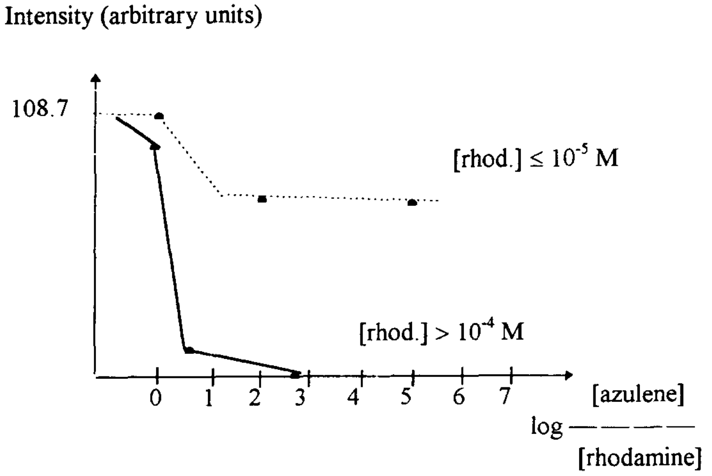


Fig. 1. Rhodamine fluorescence as a function of azulene concentration.

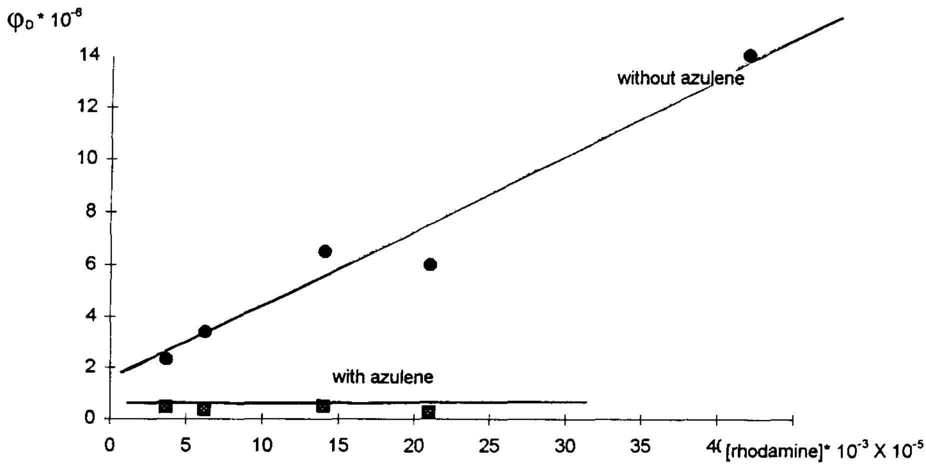


Fig. 2. Relation between the rhodamine quantum yield and its concentration.

TABLE 3
Effects of additives on the quantum yield of rhodamine photodegradation

[rhodamine] mol.l^{-1}	2.1 10^{-4}	2.1 10^{-4}	2.1 10^{-4}	2.1 10^{-4}	2.1 10^{-4}
[DABCO] mol.l^{-1}	0	2.1 10^{-3}	0	0	2.1 10^{-3}
[ascorbic acid] mol.l^{-1}	0	0	2.1 10^{-3}	0	0
[2-6 di-tert-butyl-methyl-4-phenol] mol.l^{-1}	0	0	0	2.1 10^{-3}	2.1 10^{-3}
ϕD	6.0 10^{-6}	5.7 10^{-7}	1.5 10^{-7}	4.8 10^{-7}	3.2 10^{-7}

emission. In these two experiments the influence of azulene is thus demonstrated.

When we consider the role of the azulene on the photodegradation, we must also study its action on the singlet and triplet states. The main result is the stability of the photodegradation quantum yield whatever the rhodamine concentration. If the singlet state was the predominant state involved in the photodegradation of rhodamine, the effect of azulene should provoke a large decrease of this degradation (in reference with its action on fluorescence). In fact, the result is different and for this reason, it is necessary to consider the triplet state of rhodamine as the excited state of the photodegradation.

In a previous paper [5], we investigated the photodegradation of rhodamine 640 and suggested the use of the radicals inhibitors to decrease the degradation.

We have tested three compounds, viz., DABCO, L—ascorbic acid, and 2,6 di-tert-butyl-4-methylphenol [9] (Table 3).

$$C_6H_{12}N_2 \quad C_{12}H_{14}CaO_{12}, 2H_20 \quad C_{15}H_{24}O$$

DABCO, Ascorbic acid calcium salt dihydrate serie L, 2-6-di-tert-butyl-4-methylphenol

With all these additives, a decrease of the rhodamine photodegradation quantum yield was observed but these compounds are easily degraded and their action is short. With the mixture DABCO and 2,6-di-tert-butyl-4-methylphenol, the rhodamine life-time increases just as the phenol life-time.

In the last experiment, we have a combination of the different effects of DABCO and 2,-6-di-tert-butyl-4-methylphenol. DABCO is active as triplet inhibitor while the phenol is radicals inhibitor [10].

CONCLUSIONS

When we consider the influence of azulene on the photodegradation of the rhodamine B, a decrease of the degradation kinetics is apparent. We know that azulene can quench the singlet and triplet states of rhodamine, and the inhibition of photodegradation may then be described in terms of a physical or chemical quenching of one or more of the electronically excited states ^{1}S, ^{1}T and O_2 (^{1} Δg). The inhibition of rhodamine photodegradation by azulene is due to a four bimolecular quenching process with different rate constants [11], viz.,

Transfer to azulene from rhodamine ^{1}S

$$^1S + Q \rightarrow {}^0S + {}^1Q$$

Diffusion limited oxygen quenching

$$^1S + {}^3O_2 \rightarrow {}^1T + O_2({}^{\Sigma}\varepsilon_g^-)$$

Spin limited oxygen quenching of ^{1}T

$$^1T + O_2({}^3\varepsilon_g^-) \rightarrow {}^0S + O_2({}^1\Delta_g)$$

Diffusion limited azulene

$$^1T + Q \rightarrow {}^0S + {}^1Q$$

In our experiments, we have studied the photodegradation of rhodamine at 511 nm and, at this wavelength, the photodegradation of azulene is negligible. In these conditions, this additive is very interesting, since it stabilizes rhodamine without decreasing its fluorescence in the concentration range of 10^{-5} M.

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