

# VISIBLE LIGHTS INDUCED POLYMERIZATION REACTIONS : INTERACTIONS BETWEEN ROSE BENGAL AND IRON AREN COMPLEX

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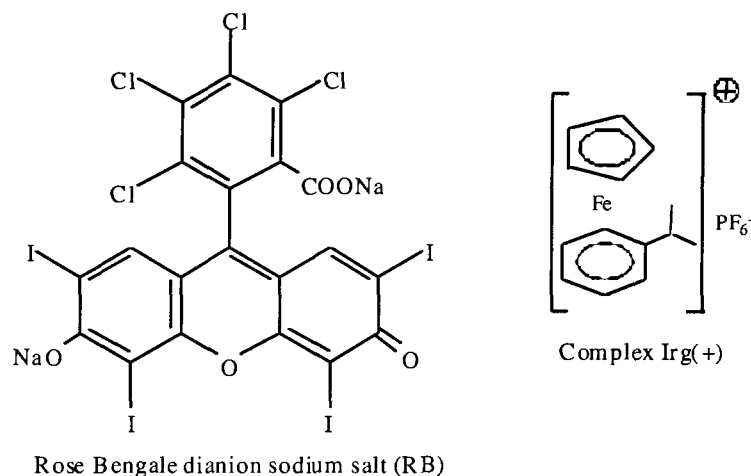
## ABSTRACT

The present paper is devoted to an investigation of the interactions between Rose Bengal (RB) and an Iron aren (Irg(+)) complex that are usable in visible light induced polymerization reactions. Steady state and flash photolysis experiments were performed in order to elucidate the nature of the intermediates formed after light excitation. A complete scheme of evolution of the excited states is discussed.

## INTRODUCTION

Rose Bengal (RB) is a xanthenic dye which is used as a photoinitiator of polymerization (1-4). The absorption domain and photochemical properties of RB make it suitable for applications in which an enhanced visible sensitivity is needed. Therefore, applications like UV-curing of paints, inks and varnishes increase the interest for such xanthenic dyes. Recently, a patent concerning a system containing a xanthenic dye as light absorber combined with an iron aren complex (Irg(+)), an amine and a hydroperoxide able to photoinitiate a polymerization in a coloured acrylic coating of up to 400  $\mu\text{m}$  thickness was described (5). The main characteristics of RB are a high absorption coefficient in the visible region and a high triplet quantum yield. The formation of ground state complexes between charged dyes like RB or eosin and organic counter ions as for example onium or N,N'-dialkylbipyridinium salts are known. The excited states of RB are easily reduced or oxidised and lead to the formation of long lived radicals which can be the starting point of further reactions. However, even in the absence of quencher the excited states of RB can lead, in competition with the known delayed fluorescence process, to the formation of semi-oxidised ( $\text{RB}^{\bullet+}$ ) or semi-reduced ( $\text{RB}^{\bullet-}$ ) dye through self-quenching or triplet/triplet annihilation.

Iron aren (Irg(+)) complexes are used as organometallic photoinitiators of polymerization. They are able to photoinitiate the polymerization of epoxides via a ligand exchange/cationic process but they are reported not to be useful with methyl methacrylate or styrene under irradiation with glass filtered light. However, in the presence of an hydroperoxide, the sensitization of the complex by RB makes that it becomes able to cure efficiently acrylic monomers by visible irradiation ( $\lambda=540\text{nm}$ ).

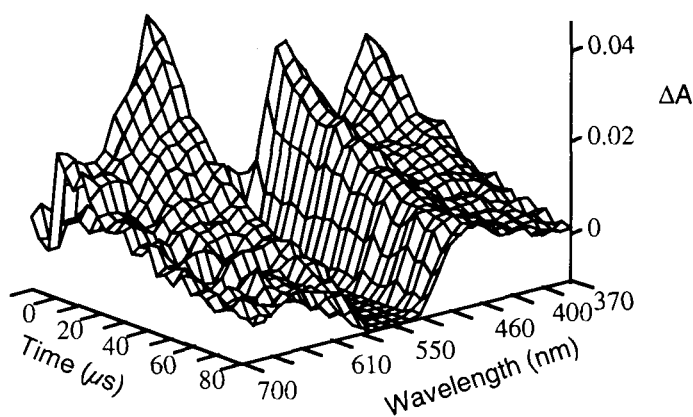


## RESULTS AND DISCUSSION

### Rose Bengal in acetonitrile/water

The fluorescence emission spectrum of RB in acetonitrile/water mixture (v/v 70/30) shows a maximum at 576 nm whereas the absorption maximum is located at 555 nm. The fluorescence lifetime was found to be 0.64 ns. The singlet energy is estimated to  $E_s = 2.21$  eV and the triplet energy to  $E_T = 1.85$  eV.

The transient absorption spectrum at low concentration of RB ( $< 25 \mu\text{M}$ ) shows three clear absorption maxima at 590, 470 and 390 nm with lifetimes of about 35, 60 and 30  $\mu\text{s}$  respectively (Figure 1) corresponding for the two first to the triplet state and  $\text{RB}^{\bullet+}$  respectively. The transient absorption of  $\text{RB}^{\bullet-}$  is located at 420nm.



**Figure 1:** Absorption changes following laser excitation of an argon saturated acetonitrile/water v:v 70:30 RB solution.

## The RB-Irg(+) system

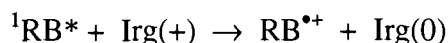
In the acetonitrile/water mixture, the UV-visible absorption spectra of RB solutions do not present significant modification upon addition of Irg(+) whereas the fluorescence spectrum only shows a slight bathochromic shift after the first addition of Irg(+).

The complex Irg(+) reacts with excited RB (both the singlet and the triplet states) with very high rate constants ( $1.9 \times 10^{11} \text{ M}^{-1} \cdot \text{s}^{-1}$  and  $5 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ ); the observed quenching rate constant for the singlet state exceeds the diffusion limit by one order of magnitude. In time resolved fluorescence quenching, the excited state lifetime is not as affected by the presence of Irg(+) as expected: the dynamic quenching rate constant determined by the lifetime quenching experiments is near the diffusion limit ( $k_q^d = 1.4 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ ) as expected for a bimolecular collision process in solution and much lower than that determined by the fluorescence intensity quenching. Moreover, the time decay curves show that the initial fluorescence intensity decreases with Irg(+) which indicates the contribution of a non molecular-diffusion limited quenching process called static quenching process.

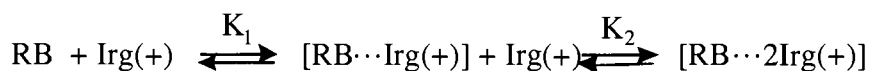
No significant changes in the transient absorption spectrum are observed, the relative intensities of the 590, 470 and 420 nm absorptions remaining nearly the same. The deactivation of the triplet state through electron transfer is effectively not energetically favoured (6) and the observed quenching must be issued from energy transfer. The lifetimes of the 470 nm and 420 nm located transients are also reduced by addition of Irg(+) with quenching rate constants of  $4.7 \times 10^9$  and  $3.9 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$  respectively. For concentrations as low as 5 mM of Irg(+), almost all the triplet and  $\text{RB}^{\bullet-}$  signals disappear and a transient absorption which cannot be that of the triplet anymore remains at 470 nm, (the absorption maximum of  $\text{RB}^{\bullet+}$ ) which means that the quenching of  $\text{RB}^*$  by Irg(+) occurs through oxidation of the former *in the singlet state*.

## The mechanism of interaction

With the knowledge of the redox and photophysical properties of RB and Irg(+) [6], both singlet energy transfer between  $^1\text{RB}^*$  and Irg(+) and electron transfer between  $^3\text{RB}^*$  and Irg(+) can be ruled out;  $^3\text{Irg}(+)^*$  can be formed by energy transfer from  $^3\text{RB}^*$ . On the other hand,  $\text{RB}^{\bullet+}$  might be issued from the reduction of  $^3\text{Irg}(+)^*$  by  $\text{RB}^*$  (singlet or triplet) following the energy transfer from  $^3\text{RB}^*$  to Irg(+) : however, at low light intensity, the reaction of  $^3\text{Irg}(+)^*$  with a second  $\text{RB}^*$  is unlikely. The singlet excited state quenching is very efficient, exceeding the diffusion limit and the intersystem crossing to the triplet state can be completely inhibited at low concentration of the ferrocenium salt. Consequently, the only important process for the interaction RB/Irg(+) is a direct electron transfer between  $^1\text{RB}^*$  and Irg(+), which is feasible on thermodynamics grounds :

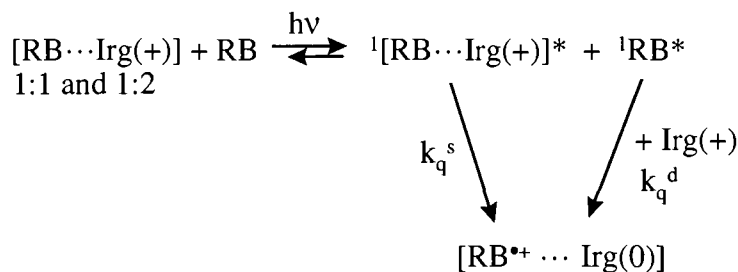


Time resolved fluorescence experiments clearly show the contribution of a static quenching process and suggest the formation of a ground state complex between RB and Irg(+) in which a diffusionless reduction of the cationic ion in the (dye/counter-ion) pair after absorption of light by the dye occurs. The contribution of a ground state complex is not surprising for a xanthenic dye and can lead to 1:1 and 1:2 complex for the RB dianion :



Preliminary results obtained in neat acetonitrile show a significant modification of the absorption of RB upon addition of Irg(+). In solution, a mixture of all the three species exists. After light absorption (scheme 1), the singlet excited state of the free and associated dye molecules is reached. Within the associated forms [RB / Irg(+)] (1:1 or 1:2), the singlet excited state of the dye is quenched with a rate constant  $k_q^s$  and leads to the formation of  $\text{RB}^{\bullet+}$  and  $\text{Irg}(0)$ . Besides the intra ion-pair reaction, the free  $^1\text{RB}^*$  can either lead to the triplet state through intersystem crossing (ISC) or can be quenched by Irg(+) through a bimolecular electron transfer process with a rate constant  $k_q^d$ . The later leads to the same product as the intra-ion pair ET, i.e.  $[\text{RB}^{\bullet+}\cdots\text{Irg}(0)]$ , which can dissociate into free species or return to the initial ground state products after back electron transfer.

#### Scheme 1:



The complexation of RB with Irg(+) will be discussed in a forthcoming paper. The 19e complex formed in the electron transfer process, hence  $[\text{Fe}^{\text{I}}\text{Cp}(\text{arene})]^0$ , is the starting point of several reaction steps involving also interactions with amines and the hydroperoxides and leads to the generation of radicals which are able to promote a polymerization reaction. Such a photoinitiating system based on RB/ Irg(+)/ amine / hydroperoxide is very efficient for the UV curing of paints usable -with sufficient pigment concentration and thickness for an adequate coverage power- in the wood furniture industry.

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