Photochemistry and photophysics of hydroxyfluorones and xanthenes [1]

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Abstract

Laser-initiated photopolymerization has opened the doors to the rapid prototyping revolution. Driven by computer control, the polymerization process can create plastic models which conform accurately to a programmed design in three dimensions. The control programs may be derived from various sources including CAD files, CT scans or other tomographic medical imaging sources such as MRI in a process called "stereolithography". Models formed by stereolithography conform concisely to a design pattern in all dimensions, and the process has shortened the time required for implementation from months to days in industries ranging from automotive and glass to medical devices.

Keywords: Hydroxyfluorones; Xanthenes

The Neckers program focuses on the processes of laser-initiated photopolymerization and associated technologies [1,2]. The overall goal is to understand the fundamentals of all steps of the complex processes from light absorption and the disposition of the excited states formed initially to the sequence of reactions leading to the solid photopolymer. An important technical aim is to relate the photophysics/photochemistry of the initiator system to the ultimate polymeric structure, and hence the physical, eventually mechanical, properties of the bulk polymer and/or shaped object, coating or composite. A critical development in the evolution of the Neckers program was his relationship with Charles Hull, the inventor of the notion of rapid prototyping and three-dimensional systems, where he, Neckers, was engaged as a consultant. Neckers and his students pioneered the use of stereolithography in medical imaging and in collaboration with Professor L.T. Andrews (Director of Imaging Analysis Laboratory, Medical College of Ohio, Toledo, OH) and his students developed the first use of photopolymerization to convert CT and MRI data to three- dimensional models for diagnosis and surgical planning [3]. An ultimate goal of this work is to form parts which can be used for complex machines or other devices, in contrast with plastic models of parts, from a computer graphic generated by CAD, CT or MRI by laser-assisted photopolymerization.

A critical part of the basic program is to develop and understand new photochemistries for use with common commercial laser systems such as laser diodes. These sources are

reliable, inexpensive and compact, and the photochemical systems which use them will be endowed with advantages in any application. To fulfill this goal, we have undertaken the development of photopolymerization processes employing visible/IR initiators. The majority of compounds which absorb visible radiation to produce the reactive intermediates responsible for the initiation of reaction chains involved in polymerization do so by means of oxidation/reduction processes. Consequently, a critical issue is the study of the electron transfer reactions of long-wavelength- absorbing dyes, most of which are bimolecular and require the presence of a partner reductant or oxidant called a coinitiator. Progress has been marked on the relationship between the photochemistry of the dye/coinitiator system and the mechanical properties of the polymers formed by the chain reaction(s) produced, and it is now possible to claim, with the developed systems, that photopolymerization initiated with visible light (with all the advantages which that entails) supersedes photopolymerization with UV light in performance for selected applications. Since an important limitation of UV-initiated polymerization is the inability to function in highly absorbing systems or in systems filled with insoluble fillers such as those which provide structural reinforcement for plastic shapes, this technical achievement affects, in particular, plans to develop a methodology for the formation of engineering materials. Using laser-initiated polymerization to make thin or thick films containing pigments of all colors has also been achieved. It is also possible to carry out polymerization in the presence of UV absorbers in the system (either adventitiously or purposefully, e.g. as antioxidants). The latter are important to

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the long-term photostability of polymeric coatings which are subject to light- induced oxidative degradation.

Our interest in visible light photoinitiators results from work on the development of xanthene dyes ($X \equiv H$, halogen) both as singlet oxygen sensitizers and as photoinitiators [4].
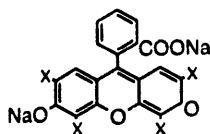
General structure of xanthene dye

We and others have specifically studied eosin ($X = Br$) as a photoinitiator [5]. Eosin's spectral properties in polar solvents such as methanol (absorption: $\lambda_{max} = 528$ nm; $\epsilon_{max} = 1.1 \times 10^5$ M^{-1} cm^{-1}; emission: $\lambda_{fl} = 547$ nm; $\phi_f = 0.59$) are such that it is almost perfectly suited as a potential initiating system for the argon ion laser ($\lambda = 514$ nm). With electron donors such as triethylamine or triethanolamine it polymerizes acrylates when irradiated and bleaches by means of known chemistry [6,7]. The mechanism involves reductive electron transfer to the dye from the amine followed by proton loss from the triethanolamine radical cation ($TEOA^{\cdot+}$). The α-amino radical ($TEOA^{\cdot}$) formed is the initiating radical.

Eosin/triethanolamine initiating systems also have certain limitations in three-dimensional imaging applications (an original visible stereolithography system used eosin/triethanolamine to initiate polymerization (Quadrax, Inc.) and the products formed were of poor resolution. Therefore as part of a program on "Photopolymerization in Three Dimensions", we sought better initiators by which the polymerization of a liquid monomer could be accurately controlled in all three dimensions x, y and z relative to an initiating laser beam of certain dimensions striking an x,y monomer surface in the z direction (laser pulse of low power).

In a project designed to obtain IR sources of singlet oxygen, Gottschalk et al. [8] turned to the cyanines which were known to absorb at much longer wavelengths than the commercial xanthenes. Although cyanines have limitations for this application, because the triplet yields are very low in polar solvents, Gottschalk found other reactions. He invented the cyanine borate visible light photoinitiators in the mid-1980s after just a few weeks on a project [9] intended to develop dyes which could be used as radical initiators at the wavelengths of the primary visible colors. (This is a classic case of so-called "indirect" technology transfer. Gottschalk, working on cyanines with the PI, found an interest in borate anions at Mead Imaging as a result of a consulting relationship Mead had at the time with Gary B. Schuster. Gottschalk's contribution was to recognize the potential of the ion pair, Cy^+, $Borate^-$.) The cyanine borates Gottschalk invented (R = alkyl, R' = alkyl) provided the basis for authentic color microcapsule color copying and printing based on the principles of "carbonless carbon paper" and developed into a color duplicating process eventually called Cycolor®.
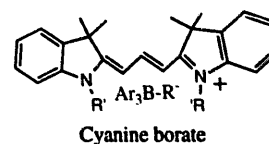
Cyanine borate

The cyanine borates have generated intense interest mostly in the patent literature and mainly from Japan [10]. They give rapid photoresponse (rapid photoresponse means different things to different groups; our goal is less than 1 mJ cm^{-2} at a single wavelength, i.e. with a laser radiation source) in microcapsules filled with a polymerizable acrylate by producing radicals by extremely rapid electron transfer from the negative borate ion to the singlet state of the cyanine cation [11]. In triphenylalkyl borates, for example, this transfer is succeeded by the loss of the alkyl radical from the oxidized borate and the formation of triphenylboron. The alkyl radical initiates polymerization. The cyanines have exceptionally high extinction coefficients, and this limits their use to applications such as imaging processes where incomplete conversion to polymer is an advantage. In the Cycolor® process, an image is formed by breaking the microcapsules, which contain dissolved acid- sensitive, leuco dyes, onto an acidic surface which usually resides on a second, partner surface called the developer layer. Photopolymerization incurred by the liquid monomers on light absorption of the appropriate wavelength hardens that particular microcapsule and prevents the development of its contents on rupture onto the acid surface.

Visible light photopolymerization, in general, offers many potential advantages over commercial UV systems. Visible sources remain simpler and easier to operate. A simple overhead projector can be used to demonstrate the use of visible polymerization systems. Relatively safe, more reliable, simpler (and less powerful) lasers are also available to produce longer wavelength light. As indicated above, most visible initiators function by electron transfer mechanisms (the light-absorbing species is either oxidized or reduced in the excited state) and a number of them produce bleached products. Bleaching provides a greater depth of polymerization with the same irradiation dose.

Our first system post-xanthene was RBAX. On a general basis RBAX is a xanthone, analogous to the thioxanthones which are common commercial UV photoinitiators. The latter are used with typical tertiary amine accelerators and therefore can be described, as can benzophenone/Michler's ketone, as electron transfer UV photoinitiators. In other words, the first step in the mechanism of their initiating polymerization is electron transfer from a donor, e.g. a tertiary amine, to a thioxanthone excited state. Based on the known photoreduction chemistry of rose bengal (RB), we anticipated that electron transfer would reduce the xanthene skeleton of RBAX and that the radical anion thence formed might decay by the elimination of an acetoyl radical. Acetoyl is analogous to benzoyl which is the radical which initiates chains in the case of most Norrish type I UV photoinitiators, i.e. benzoin
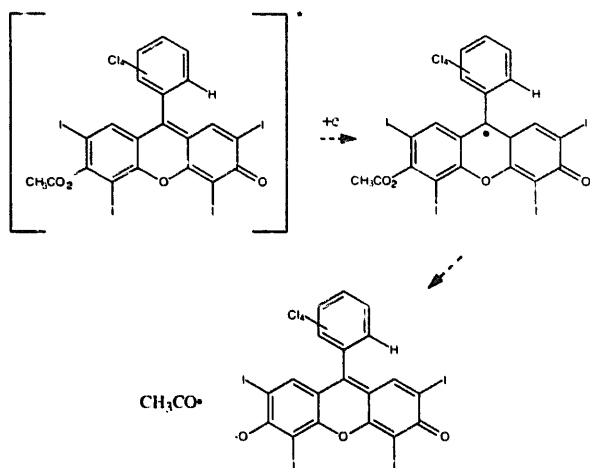
Scheme 1. Photoreduction of RBAX.

ethers or acetophenone acetals. The proposed scheme is shown in Scheme 1.

The spectral shape and molar absorptivity of RBAX are similar to those reported for the non-polar derivatives of RB [12]. Irradiation of RBAX (1.19×10^{-4} M) in the presence of triphenyl n-butyl borate ion (1.89×10^{-3} M) results in the bleaching of RBAX and the appearance of an absorption peak at 560 nm. This wavelength corresponds to λ_{max} for decarboxylated RB. Fluorescence measurements show that the excitation spectrum is identical with the absorption spectrum of decarboxylated RB. The bleaching products have not been isolated. Based on the known products for the bleaching of RB under reductive conditions and the fact that the oxidation of the triphenyl n-butyl borate ion generates butyl radical, we expect the formation of the coupling product between RBAX and the butyl group. Therefore the reaction can be represented as

$$\text{RBAX} + \text{Bo}^- \xrightarrow{h\nu} \text{Bleaching product} + \text{RB} + \phi_3\text{B} \qquad (1)$$
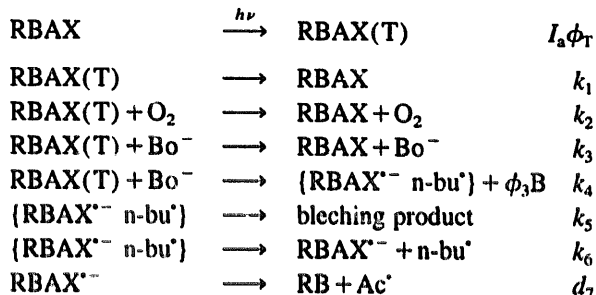
The quantum yields of RBAX bleaching and of RB generation were determined by measuring the decrease in the absorption at 486 nm and the increase in absorption at 560 nm as a function of the light intensity and Bo$^-$ concentration. A summary of our results can be given as follows:

(a) the rates of RBAX bleaching, $-d[\text{RBAX}]/dt$, and the generation of decarboxylated RB, $d[\text{RB}]/dt$, vary linearly with the absorbed light intensity in the range 1.0×10^{-5} to 1.2×10^{-4} einstein $l^{-1} s^{-1}$;

(b) $\phi(\text{RB})/\phi(-\text{RBAX})$ is (8.6 ± 1.2) $\times 10^{-2}$, independent of the light intensity, Bo$^-$ concentration (1.0–24 mM) and the presence of air;

(c) in argon-saturated solution and $[\text{Bo}^-] = 1.89 \times 10^{-3}$ M, the quantum yield of bleaching of RBAX is 0.31.

The quantum yield of RBAX reduction is 0.39 ± 0.03 at infinite Bo$^-$ concentration. In view of the low Bo$^-$ concentrations required to observe the photoreduction, we conclude that the reactive excited species is the triplet state of RBAX. Measurements of the lifetime of the RBAX triplet by laser

flash photolysis yield values of 3.64 μs in argon-saturated solution and 288 ns in the presence of air (the triplet of RBAX was monitored at 610 nm; we will report our complete flash photolysis study in a future publication). These lifetimes are independent of the energy of the laser pulse (0.2–3 mJ per pulse) and of the concentration of RBAX ground state in the range 1.74×10^{-5} to 2.23×10^{-4} M. A mechanism consistent with these observations is presented in Scheme 2, where n-bu$^•$ and Ac$^•$ represent n-butyl and acetyl radicals respectively

RBAX	$\xrightarrow{h\nu}$	RBAX(T)	$I_a\phi_T$
RBAX(T)	$\longrightarrow$	RBAX	k_1
RBAX(T) + O$_2$	$\longrightarrow$	RBAX + O$_2$	k_2
RBAX(T) + Bo$^-$	$\longrightarrow$	RBAX + Bo$^-$	k_3
RBAX(T) + Bo$^-$	$\longrightarrow$	{RBAX$^{•-}$ n-bu$^•$} + ϕ_3B	k_4
{RBAX$^{•-}$ n-bu$^•$}	$\longrightarrow$	bleaching product	k_5
{RBAX$^{•-}$ n-bu$^•$}	$\longrightarrow$	RBAX$^{•-}$ + n-bu$^•$	k_6
RBAX$^{•-}$	$\longrightarrow$	RB + Ac$^•$	d_7

Scheme 2. Overall mechanism for the reduction of RBAX by borate.

From laser flash photolysis measurements we obtain $k_1 = 2.78 \times 10^5$ s^{-1} and $k_1 + k_2[\text{O}_2] = 3.47 \times 10^6$ s^{-1} in air. The quantum yields are given by

$$\phi(-\text{RBAX}) = \phi_T k_4[\text{Bo}^-]/[k_1 + k_2[\text{O}_2] + (k_3 + k_4)[\text{Bo}^-]],$$

$$\phi(\text{RB}) = (k_5/k_5 + k_6)\phi(-\text{RBAX}) \qquad (2)$$

The observation that the rate of RB generation varies linearly with the absorbed light intensity provides evidence that the radicals RBAX$^{•-}$ and n-bu$^•$ do not undergo significant recombination after dissociation of the geminate pair. Similarly, the lack of dependence of $\phi(\text{RB})/\phi(-\text{RBAX})$ on the presence of air indicates that RBAX$^{•-}$ is not significantly quenched by oxygen during the lifetime of the radical. The evidence for the lack of oxygen quenching of the geminate pair is presented below. Assuming that the oxidation of RBAX$^{•-}$ by oxygen is diffusion controlled, we obtain a minimum value for k_7 of 4×10^8 s^{-1}.

The ratio $\phi(\text{RB})/\phi(-\text{RBAX})$ is equal to (8.6 ± 1.2) $\times 10^{-2}$. From this value, we derive $k_5/k_6 = 10.6 \pm 1.6$. We identify A and B as follows

$$A = \phi_T k_4/(k_3 + k_4) = 0.39 \pm 0.03$$

$$B = (k_1 + k_2[\text{O}_2])/(k_3 + k_4) = (4.16 \pm 0.21) \times 10^{-3} \text{ M}$$

By introducing the lifetime of the RBAX triplet in the presence of air, we derive

$$k_3 + k_4 = (8.35 \pm 0.42) \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \qquad (3)$$

In argon-saturated solution and for $[\text{Bo}^-] = 1.89 \times 10^{-3}$ M, the quantum yield of consumption of RBAX is 0.31. From this value, we calculate $\phi_T k_4/(k_3 + k_4) = 0.37$ in argon-saturated solution, and conclude that the geminate pair (see Scheme 1) does not react with oxygen, as deactivation of the geminate pair will affect the photoreduction quantum yield at infinite borate concentration.

Table 1
Properties of example fluorones

Property	DIBF	TIHF	TIHCF
λ_{max} (nm) (ϵ) [a]	470 (30200)	536 (92600)	638 (80000)
λ_{fl} (nm) (τ, ns); ϕ	Broad (–); 0.02	548 (0.65); 0.13	654 (0.69); 0.02
λ_{ph} (nm) (77 K); ϕ	570	676 (0.87)	777 (0.99)
$E(D^-/D)$ (V) [b]	–0.90	–0.99	–0.57
$E(D/D^+)$ (V)	1.40	1.34	–
Red.; k_q (m^{-1} s^{-1}) [c]	1.2×10⁸ (a) 6.7×10⁷ (b)	2.4×10⁷	8.9×10⁸
Ox.; k_q (m^{-1} s^{-1}) [d]	0	≈7×10⁷	–
Air; k_d (m^{-1} s^{-1})	2.5×10⁹		

[a] EtOH.
[b] Vs. SCE.
[c] [Dye] = 10⁻⁵ M; [ArNR₂] = 10⁻³ M; (a) ArNR₂; (b) Ar₃BR⁻ (R = alkyl; Ar = Ph).
[d] [Dye] = 10⁻⁵ M; [Ar₂I⁺, SbF₆⁻] = 10⁻³ M.

Although both xanthenes and cyanine borates have extensive histories, the advantages of visible light polymerization are not optimized by either group of compounds. Xanthenes have serious solubility problems in most organic monomers. Cyanine borates offer a wide range of colors and are exceptional for photographic applications, but often produce poly(polyolacrylate) of low mechanical strength. They also tend to remain deeply colored after polymerization, thus precluding their use in many situations. RBAX gave us a pattern to follow, but it had a number of problems as well as opportunities which needed to be optimized. In addition, we were really interested in longer wavelength absorbers. In order to broaden the versatility of visible initiators for applications in which polymer properties are a major issue, we developed a new series of initiators, the fluorones, and found the conditions in which they would form polymers with properties comparable with those formed using commercial UV initiator systems. The photoreduction and photooxidation reactions of the fluorones can be used to initiate polymerization, depending on the coinitiator partner. In the presence of appropriate electron donors, such as tertiary amines, fluorones are reduced in a bimolecular electron transfer reaction. Electron transfer from the amine to the excited triplet state of the dye forms the dye anion radical and the amino cation radical. The amino cation radical rapidly releases a proton, which is transferred to the anion radical, yielding a neutral dye and amino radicals, the latter initiating free radical polymerization [13]. This is a critical achievement of the work. Approximately 35 new dyes in the basic fluorone series were synthesized to accomplish this objective [14]. Fluorones differ from the xanthenes in that the xanthenes have an aromatic group, gen-

erally substituted with a carboxylic acid, at C-9. The structure of the parent xanthene, fluorescein, is shown.

Fluorescein
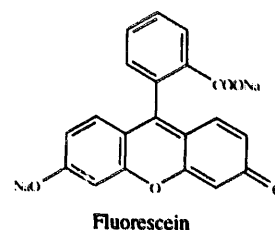
This minor structural difference has important implications on the efficiency of electron transfer and the subsequent chemistry as well as on many other chemical properties. This substitution pattern also offers the flexibility of additional substitution at the 9-position on the ring system (Table 1).

By virtue of this, groups which enhance the delocalization of charge over the aromatic skeleton yield fluorones whose absorption maxima are shifted substantially towards the red. The observation [7] that the fluorones bleach much more rapidly than the xanthenes in the presence of agents which reduce their excited states, and form strong photopolymers much more rapidly in standard acrylate systems than any related visible initiator composition, has led to an even greater interest in their chemistry. Fluorone bleaching is the result of the neutralization of the anionic, phenolic site, produced by photoreduction of the dye triplet by cations obtained on oxidation of a partner electron transfer donor, and this enhances the properties of the polymer in most cases. For example, it is productive in subsequent polymer-forming steps, rather than detrimental, as is the case with bleaching of comparable

cyanines. The fluorones [15], when reduced by dialkylanilines, give two products

(4)

R = alkyl, R' = H, ArN(CH₃)CH₂-
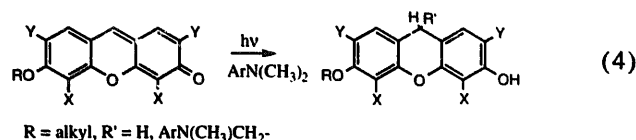
We have concentrated our mechanistic studies on three fluorone dyes, each of which targets a line of a common commercial laser [16]. (The reasons for selection include the solubility in a variety of monomer systems, electron transfer characteristics, bleaching rates, ease of use, ease of synthesis, stability when formulated in prepolymer mixtures, etc. The laser lines targeted are the 488 and 514 nm lines of the argon ion laser and the 632 nm line of the He/Ne laser.) The critical spectroscopic parameters and quenching constants measured by flash spectroscopy are given in Table 1 [17]. Excitation of each dye, 2,4-diodo-6-butoxy-3-fluorone (DIBF), 2,4,5,7-tetraiodo-6-hydroxy-3-fluorone (TIHF) and 9-cyano-2,4,5,7-tetraiodo-6-hydroxy-3-fluorone (TIH-CF), gives, after intersystem crossing, high yields of triplets. The triplets, in turn, react with either amines or borate anions to give radicals which initiate polymerization with high efficiency. There is no evidence to indicate that DIBF triplets react with oxidizing agents, such as diphenyliodonium hexafluoroantimonate (ϕ_2I^+, SbF_6^-), but the triplets of TIHF and TIHCF do.

The flash photolysis results confirm that the photoreduction of DIBF in the presence of an electron donor, tertiary amine (DIDMA) or borate salts (BORATE), is a one-electron transfer process as shown in Schemes 3 and 4 (see below). Electron transfer from the borate anion or amine results initially in the DIBF radical anion (DIBF⁻) and the boranyl radical pair in the first case and DIBF⁻ and the amino radical cation pair in the second. The transient spectra in the BORATE case show that DIBF⁻ is the only product obtained after quenching of the DIBF triplet. The formation of the radical anion was observed on a nanosecond time scale and at the same rate as the triplet decay. The radical anion decay did not regenerate the dye as should be the case if back electron transfer occurs. This information proves that boranyl radical dissociation (k_d, Scheme 3) in this system is very fast and occurs on a shorter time scale before back electron transfer. Chatterjee et al. [18] reported that, in the cyanine/borate system, the boranyl radical dissociation to give triphenylborane and alkyl radicals is faster than the back electron transfer, depends on the stability of the alkyl radical formed and the dissociation is irreversible. For the specific cyanine/triphenylbutylborate case, they found that dissociation of the boranyl radical is very efficient (greater than 10^{11}). Assuming that $k_{-et} \approx 0$ (Scheme 3) and based on the observation that the rate of radical formation is the same as the rate of triplet decay, we estimate the electron transfer rate in this system to be the same as the measured triplet quenching rate which is 6.71×10^7 s⁻¹. This result is in good agreement with the
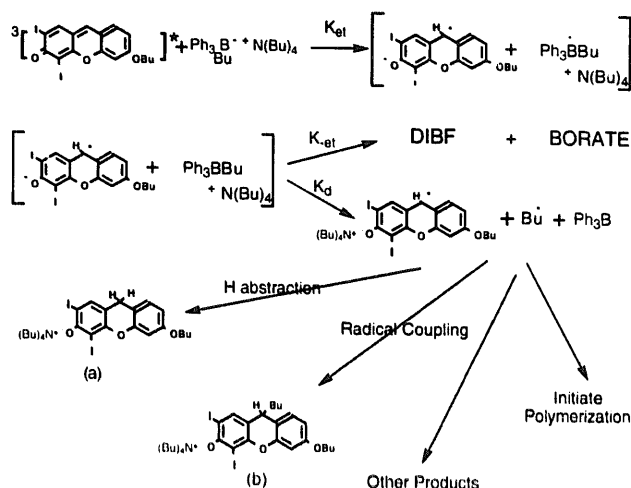
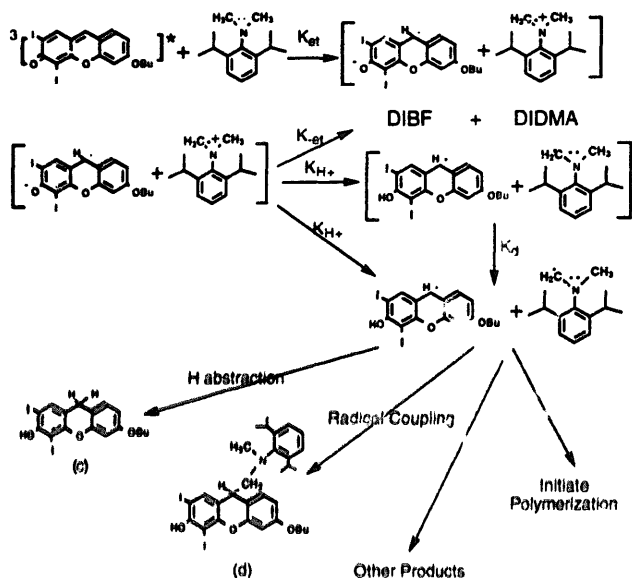Scheme 3. Proposed mechanism in the case of DIBF and BORATE.

values obtained in previous work with dye/amine systems, but is very low compared with the intramolecular electron transfer rate ($k_{et} \approx 10^{11}$ s⁻¹) obtained for cyanine/borate systems (Scheme 3).

In the DIBF/DIDMA case, we were unable to observe the dye radical anion on a nanosecond time scale. Instead the neutral dye radical (DIBF·) was obtained. Scheme 4 describes the proposed mechanism in the present case. After the initial electron transfer from the amine nitrogen to the dye triplet, DIBF⁻ and the amino cation radical are obtained. The dye radical anion has an oxygen radical center at the 6-position, which promotes rapid proton transfer from the carbon α to the nitrogen in the amino cation radical [19] to give the neutral dye radical and the amine radical. In the presence of monomer, the amine radical and, to some extent, the dye radical initiate polymerization. The protonation of the dye radical anion can happen inside or outside the solvent cage as shown in Scheme 4. In either way it is too fast (large k_H^+ and k_d) to measure on a nanosecond time scale. Also, in this case, the radical formation rate is the same as the rate of dye triplet decay and the radical decay does not regenerate the dye. Therefore, and similar to the BORATE case, we estimate the electron transfer rate to be the same as the triplet quenching rate, 1.21×10^8 s⁻¹. This rate is 1.8 times faster than in the BORATE case and 5 times faster than in the similar system studied previously (TIHF/amine) (Scheme 4).

The free energy change ΔG_{et} for the electron transfer process, calculated using the Rehm–Weller [20] equation

$$\Delta G_{et} = E_{ox}(D/D^{·+}) - E_{red}(A^{·-}/A) - E_{0-0}^T - Ze^2/\epsilon a \qquad (5)$$

where $E_{ox}(D/D^{·+})$ is the oxidation potential of the electron donor (DIDMA or BORATE), $E_{red}(A^{·-}/A)$ is the reduction potential of the electron acceptor (DIBF) and E_{0-0}^T is the triplet excitation energy, correlates very well with the obtained electron transfer rates. $Ze^2/\epsilon a$ is the coulombic energy, which is the free energy gained by bringing the two radical ions to an encounter distance a in a solvent with a dielectric constant ϵ. The reduction potential of DIBF meas-
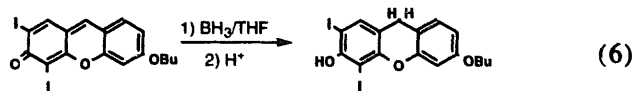
DIBF + DIDMA

H abstraction

Radical Coupling

(c)

(d)   Other Products

Initiate
Polymerization

Scheme 4. Proposed mechanism in the case of DIBF and DIDMA.

1) BH₃/THF
2) H⁺   (6)

The bleached products 1 and 2 decrease after 72 h, while the concentration of DIBF recovers. If 1 is the dihydro derivative, 2 is probably the cross-coupled product (d). Phillips and Read [22] reported that, in the photoreduction of the eosin analog by tribenzylamine, 52% yield of the dihydro derivative and 39% yield of the cross-coupled product were obtained. In our case it seems that the cross-coupled bleached product is the principal product. However, in agreement with Phillips and Read [22], we also observe that the cross-coupled product (d) is oxidized mainly re- forming the initiator.

Comparison of the two cases, DIBF + DIDMA and DIBF · BORATE, after irradiation shows that, in the case of BORATE, no peaks are detected at higher rt range. However, the BORATE peak decreases, and peaks with the same rt are observed at longer wavelengths. The UV–visible absorption spectrum of the new peaks is very similar to the absorption spectrum of the anionic form of DIBF which also suggests that this form has an ionic (salt) structure as proposed in Scheme 3.

Small amounts of phenol and biphenyl obtained after irradiation in the BORATE case are probably a result of the reaction of oxygen with triphenylborane [21], as biphenyl and phenol are found in larger amounts in the mixture than triphenylborane.

Re-oxidation of the quinomethine reduced products (a), (b), (c) and (d) will regenerate the original dye, resulting in a colored solution, and is dependent on the polarity of the medium. In acetonitrile solution and in most of the photopolymer formulations, it is observed that color recovery is fast when (c) and (d) are the reduced products, but very slow when (a) and (b) are the reduced products. This is reasonable since the re- oxidation/deprotonation will be easier from the quinomethines (c) and (d) compared with the ammonium salts (a) and (b) in the same conditions.

ured by square-wave voltammetry [21] in acetonitrile is −0.9 V (vs. SCE). The triplet excitation energy determined from the phosphorescence spectrum is 2.3 eV. The literature reported oxidation potentials for similar borates and amines are approximately +0.7 V and +0.5 V respectively. Assuming that the coulombic energy is too small, the calculated ΔG_{et} values are −0.7 eV for the BORATE case and −0.9 eV for the DIDMA case, compared with −0.36 eV, the reported result for TIHF/amine from previous work.

The fate of the radical anion DIBF⁻ formed in the BORATE case and the neutral radical DIBF formed in the DIDMA case determines the final bleached products observed in both systems. This has a major effect on the color of the solution formed. In the DIBF/DIDMA solution, after the solution has been bleached by steady state irradiation, there is a relatively fast recovery of DIBF color (absorption). However, almost no recovery is found in the DIBF/BORATE solution. When OPPI is added to the solutions color recovery is also obtained in the BORATE case.

HPLC analysis of the bleached products supports the mechanisms proposed. In the BORATE case, the ammonium cation (the counterion of the borate salt) neutralizes the oxygen at the 6-position in the dye radical anion giving an ammonium "salt" radical, which abstracts a hydrogen atom from the solvent or couples to the butyl radical to give the reduced quinomethine ammonium salts (a) and (b). In a similar way, the neutral radical in the DIDMA case can give the quinomethines (c) and (d).

After irradiation of DIBF + DIDMA, three bleached products are obtained. One of these (bleached product 1) is confirmed to be the dihydro reduced form (c) as proposed in Scheme 4. The dihydro derivative (c) can be obtained by reducing DIBF chemically

Conclusions

Photoreduction of xanthenes, modified xanthenes and fluorones leads to radicals when both aromatic amines and triarylalkyl borate salts are used as reducing agents. Triplet quenching is the primary pathway converting the dye excited states to radical anions. Oxidation of the partner produces radicals by a series of routes. Mechanistic details and product study results have been reported.

Acknowledgements

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