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Journal of Photochemistry and Photobiology A: Chemistry 112 (1998) 173–178

Journal of Photochemistry and Photobiology A:Chemistry

A novel pathway to photoinduced colour formation of colourless fluorane dye using iodonium salts as activators

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Accepted 27 August 1997

Abstract

A photoinduced colour formation system consisting of fluorane dye (FR) and iodonium salt was investigated. The thermodynamic data indicate that the photoreaction of colour formation mainly occurs via an electron transfer pathway. The processes of electron transfer colour formation were proposed by separating and analysing the photoproducts. On irradiation, the excited fluorane dye and iodonium salt may undergo electron transfer to give a fluorane radical ($FR^{\cdot +}$) and diphenyliodonium radical ($^{\cdot}IPh_2$). The latter rapidly decomposes to a phenyl radical ($Ph^{\cdot}$) and iodobenzene, and the ring-opened coloured forms may be subsequently created via two pathways: abstraction of hydrogen by the $FR^{\cdot +}$ radical intermediate or coupling between $FR^{\cdot +}$ and $Ph^{\cdot}$. The acidic ring-opened coloured form from the abstraction of hydrogen is predominant, and easily undergoes a colour disappearance reaction in non-polar solvents or basic medium, but the structure of FR-Ph from radical coupling possesses good stability. In order to improve the solubility of the iodonium salt, several diaryliodonium salts containing different flexible phenolic chains or counterions were used as activators. The influences of these two factors on colour formation were studied; the results demonstrate that the former has no distinct effect on the rate of colour formation or maximal optical density at 580 nm, whereas the latter has a significant effect. The influence of concentration was also studied.

Keywords: Colour formation; Electron transfer; Fluorane dye; Iodonium salts

1. Introduction

The development of organic photoinduced colour formation systems started in the early 1960s. Several radical imaging systems [1–3] using halohydrocarbons as photosensitizers have been established by Horizon Research Inc., e.g. aromatic amines/tetrabromomethane, indole/tetrabromomethane and crystal violet/tetrabromomethane. The principles of these imaging systems are based on the direct or indirect interaction of the active radicals generated from the photolysis of halohydrocarbons with the colourless dye molecules to create coloured forms. Although these imaging methods may offer feasible high resolution, problems such as the easy volatility, toxicity and undesirable background colour of halohydrocarbons, have limited their practical applications. Therefore it is necessary to develop new photoinduced colour imaging systems using activators other than halohydrocarbons.

Fluorane leuco dyes are a type of important functional dye which have been widely used as pressure- and thermo-sensitive dyes for carbonless paper and facsimile systems. Usually in the presence of acidic developers, such as phenolic compounds, colourless fluorane undergoes a ring opening reaction to form the corresponding highly coloured fluorane cation; due to the different substituents in the xanthene skeleton, various colours, e.g. red, green, yellow and black, can be tuned [4,5]. To a certain degree, this acid-induced colour development reaction can be attributed to an electron transfer process; thus the fluorane lactone itself can be regarded as an electron donor with a dialkylamino group, an electron-donating substituent, in the skeleton. According to the principles of photoinduced electron transfer, the choice of an appropriate electron acceptor as activator makes it possible to realize photoinduced colour formation for this type of fluorane lactone. Onium salts, including iodonium and sulphonium salts, have low negative reduction potentials, and usually serve as electron acceptors in dye-sensitized photopolymerization [6–8]. Therefore, the photoinduced colour development system consisting of colourless fluorane and iodonium salt was investigated and a possible mechanism was proposed.

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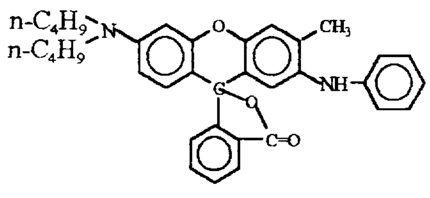
PII S1010-6030(97)00259-1

2. Experimental details

Fluorane leuco dye (FR) was provided by Yamada Chem. Co. Ltd. and purified by recrystallization from benzene. Diphenyliodonium tetrafluoroborate (DPIOB), [4-[(butyloxyl)phenyl]phenyl]iodonium hexafluorophosphate (BPPIP), [4-[(octyloxyl)phenyl]phenyl]iodonium tetrafluoroborate (OPPIB), [4-[(octyloxyl)phenyl]phenyl]-iodonium hexafluorophosphate (OPPIP), [4-[(octyloxyl)phenyl]phenyl]iodonium hexafluoroantimonate (OPPIA) and [4-[(dodecenyloxyl)phenyl]phenyl]-iodonium hexafluorophosphate (DPPIP) salts were synthesized according to the literature [9,10]. Other reagents were of analytical grade and were used as purchased. The photoreaction experiments were carried out in an apparatus equipped with a 400 W high pressure mercury lamp; the light was filtered by a $CoCl_2$/HCl/alcohol filter solution [11] (transmitting wavelength range, 260–460 nm) and the light intensity reaching the samples was 6.3 mW cm^{-2}. The nonvolatile products of the dye moiety were separated by a chromatographic column using ethyl acetate ester/petroleum ether (5 : 1, v/v) as eluent. Gas chromatography/mass spectrometry analyses were performed on a Finnigan 4012C system. The redox potential of colourless fluorane (FR) was measured on a model 273 EG&G Princeton Applied Research potentiostat/galvanostat. UV–visible absorption and fluorescence emission spectra were recorded on a Hitachi 557 UV–visible spectroscopy photometer and a Hitachi MPF-4 fluorometer respectively. The energy of the excited singlet state of fluorane was determined from its absorption and fluorescence emission spectra. IR spectra were measured on a Perkin–Elmer 983G infrared spectrophotometer.



(FR)

3. Results and discussion

3.1. Studies of photoinduced colour formation

For the reaction system consisting of diphenyliodonium salt (DPIOB) and fluorane lactone (FR), according to their redox potentials ($E_{ox} = -0.2$ V (DPIOB) [12] and $E_{red} = 0.83$ V (FR)) and the energy of the excited singlet state of FR ($E_s = 290.1$ kJ mol^{-1}), the free energy change of electron transfer (ΔG) can be calculated: $\Delta G = 99.3$ kJ $mol^{-1} > 0$ in the ground state, whereas $\Delta G^* = -190.8$ kJ $mol^{-1} < 0$ in the excited state. Therefore the thermodynamic data indicate that the FR/DPIOB system possesses a desirable dark stability and a high driving force of photoreaction.

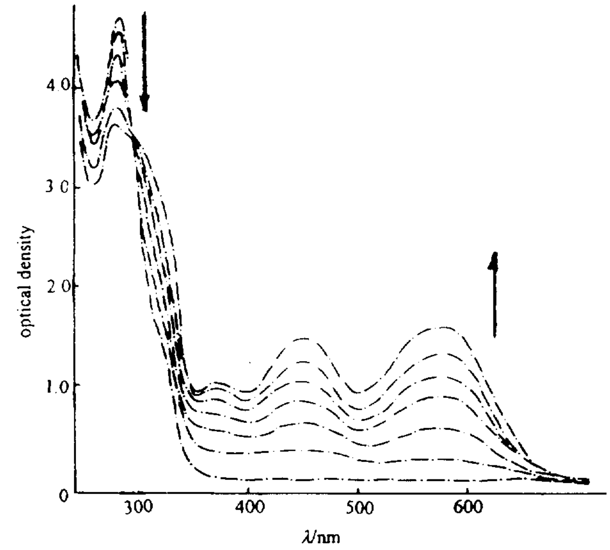


Fig. 1. Changes in the absorption spectrum of the FR/DPIOB system with irradiation time in acetonitrile; |FR|, 10^{-4} M; |DPIOB|, 10^{-4} M.

Both FR and DPIOB have no absorption in the visible region, but their UV absorptions are observed around 280 nm ($\epsilon_{max} = 3.3 \times 10^4$ mol^{-1} l cm^{-1}) and 228 nm ($\epsilon_{max} = 1.2 \times 10^4$ mol^{-1} l cm^{-1}) respectively. On exposure to UV light, the solution of FR/DPIOB exhibits a black colour rapidly. From Fig. 1, it can be seen that the two absorption peaks ($\lambda_{max} = 460$ nm and 580 nm) steadily increase with increasing irradiation time; simultaneously, the UV absorption ($\lambda_{max} = 280$ nm) gradually decreases. Because the absorption positions and shapes of the FR coloured form in the presence of DPIOB resemble those of the usual acid-induced (e.g. acetic acid) coloured form, it is reasonable to suggest that a ring opening colour development reaction may be taking place.

Obviously, irradiation with a high pressure mercury lamp will excite FR and DPIOB simultaneously; therefore the colour formation of FR/DPIOB may occur via two possible pathways: electron transfer from excited FR and DPIOB or proton transfer from the photolysis of DPIOB [13]. To distinguish between these two possible pathways, the $CoCl_2$/HCl/alcohol filter solution (transmitting wavelength range, 260–460 nm) was placed in the irradiation apparatus to avoid the direct photolysis of DPIOB. Fig. 2 shows that the colour formation of FR/DPIOB can also occur on exposure to light of 260–460 nm, and that the rate of colour formation decreases slightly compared with that on direct irradiation with the same light intensity. In addition, because the energy of the FR excited state is lower than that of DPIOB, it is not possible for energy to be transferred to DPIOB from excited FR, but energy can be transferred to FR from excited DPIOB. This indicates that, although the acid generated from the photolysis of DPIOB may induce ring opening colour formation, the photoinduced electron transfer of FR/DPIOB initiated by the excitation of FR is a major pathway to colour formation.

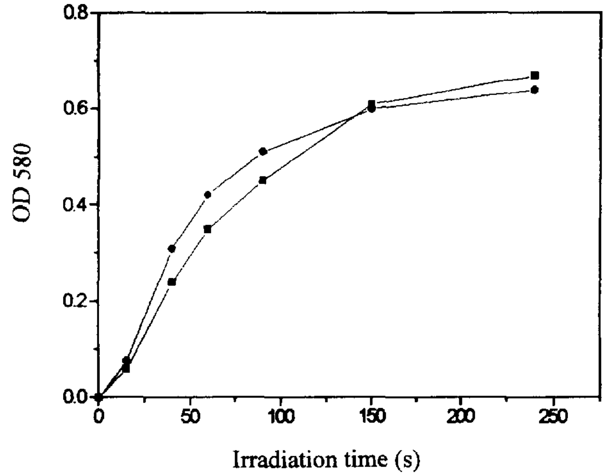


Fig. 2. Comparison of colour formation of FR/DPIOB on irradiation at different light wavelengths at the same light intensity; [FR], 10^{-4} M; [DPIOB], 10^{-4} M; acetonitrile; ●, direct irradiation; ■, with filter solution (260–460 nm).

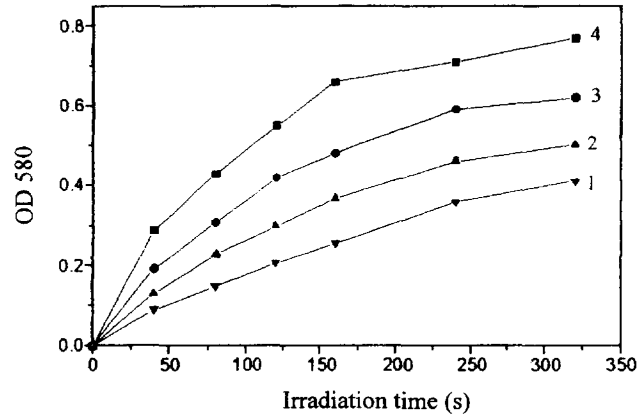


Fig. 3. Effects of solvent polarity on the photoinduced colour formation of the FR/DPIOB system; [FR], 10^{-4} M; [DPIOB], 10^{-4} M; solvent: 1,4-dioxane/acetonitrile; acetonitrile (vol.%): (1) 20; (2) 40; (3) 80; (4) 100.

Table 1
Absorption spectral data of diaryl iodonium salts containing phenolic ether chains

$\mathrm{Ph-\overset{+}{I}-PhO-C_nH_{2n+1}}$		X^-	λ_{max} (nm)	$\epsilon_{max} \times 10^{-4}$ (M^{-1} cm^{-1})
BPPIP	$n=4$	PF_6^-	246	1.10
OPPIB	$n=8$	BF_4^-	245	1.23
OPPIP	$n=8$	PF_6^-	248	1.19
OPPIA	$n=8$	SbF_6^-	248	1.44
DPPIP	$n=12$	PF_6^-	250	1.21

Further support for electron transfer is obtained from the synergistic effect of the solvent polarity on the photoreaction of FR/DPIOB. Fig. 3 shows the absorption at 580 nm as a function of irradiation in different mixtures of acetonitrile and 1,4-dioxane. It indicates that the rate of colour formation of FR/DPIOB accelerates following an increase in the solvent polarity, indicating that a strongly polar solvent is favourable for the separation of the radical pair ($FR^{\cdot +}$/$DPIOB^{\cdot}$) generated by electron transfer and inhibits back electron transfer.

Since diphenyliodonium salts are a type of organic salt, poor solubility is a common problem whether they are used as photoinitiators [10,14] or as colour developers. However, it can be readily improved by introducing a flexible chain in the phenyl ring or increasing the bulk of the counterions [10]. Therefore, several diaryliodonium salts containing phenolic ether chains of various lengths and different counterions were synthesized (see Table 1) and the effects of these two factors on colour formation were studied.

From Fig. 4, it can be seen that, when a phenolic ether chain is introduced into one of the phenyl rings of diphenyliodonium tetrafluoroborate salt (OPPIB), the rate of colour formation and the maximal optical density at 580 nm decrease slightly in comparison with the results obtained for non-substituted DPIOB. The reason for this phenomenon is that the electron-donating property of the phenolic ether results in a decrease in the electronegativity of the iodonium salt. However, different chain lengths (BPPIP, OPPIP, DPPIP) have

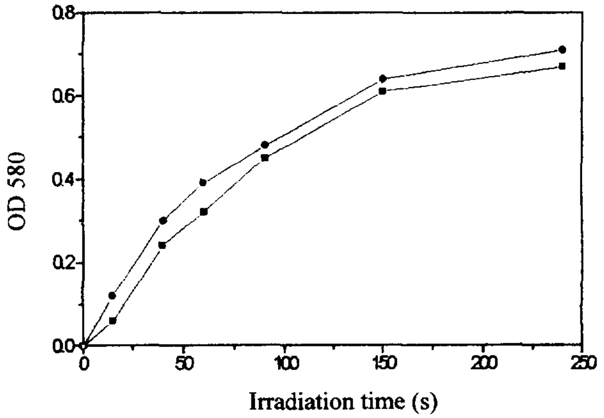


Fig. 4. Comparison of colour formation of FR/DPIOB with FR/OPPIB; [FR], 10^{-4} M; [onium], 10^{-4} M; acetonitrile; ●, FR/DPIOB; ■, FR/OPPIB.

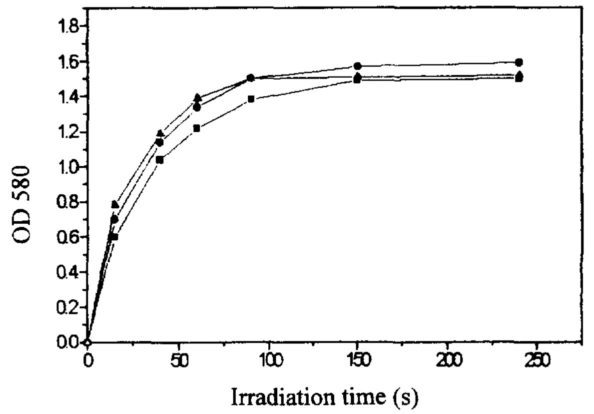


Fig. 5. Effect of different chain length of iodonium salt on the photocolour formation; [FR], 10^{-4} M; [onium], 10^{-4} M; acetonitrile; ■, FR/BPPIP; ●, FR/OPPIP; ▲, FR/DPPIP.

no significant influence on colour formation (see Fig. 5). These iodonium salts have a similar structure and electric properties.

With regard to the influence of the counterions of the iodonium salts on colour formation, different results are obtained. As shown in Fig. 6, when different counterions (BF_4^-, PF_6^-, SbF_6^-) are used with 4-[(octyloxy)-phenyl)phenyl]iodonium cation (OPPI), the rate of colour formation and the maximal optical density at 580 nm increase in the order $BF_4^- < PF_6^- < SbF_6^-$. This indicates that the coloured form generated from the photoreaction of FR with the iodonium salt is an acidic ring-opened structure (same as the acid-induced ring-opened structure). This acidic coloured form is very sensitive to the acidity of the medium as a result of the reversible equilibrium between the coloured and colourless forms. Because the ionic bulk increases in the order $BF_4^- < PF_6^- < SbF_6^-$ [15], the ability to combine with the cation and proton gradually decreases, and thus the larger the bulk of the counterion, the higher the reactivity of the iodonium cation and the more stable the coloured form.

For a bimolecular photoreaction, the concentrations of donor and acceptor also influence the reaction. From Fig. 7, it can be seen that, at constant FR concentration (10^{-4} mol l^{-1}), the rate of colour formation and the maximal optical density decrease with decreasing OPPIP concentration; when the OPPIP concentration is below 10^{-5} mol l^{-1}, almost no colour formation is observed. At low OPPIP concentration, the probability of effective collision between the excited FR and OPPIP molecules decreases greatly within the short lifetime of the excited state.

Fig. 8 shows that, when the OPPIP concentration is kept constant (10^{-4} M) and the FR concentration is varied, the absorption at 580 nm changes as a function of the irradiation time. At low FR concentration, no colour formation takes place; the rate of colour formation and the maximal optical density increase as the FR concentration is increased, but decrease at high concentration (above 10^{-3} M). This is due to the high extinction coefficient of FR: a high FR concentration may cause an inert light-screening effect which accelerates the self-quenching of the excited molecules and the deactivation of the intermediates, finally leading to a decrease in the reaction rate.

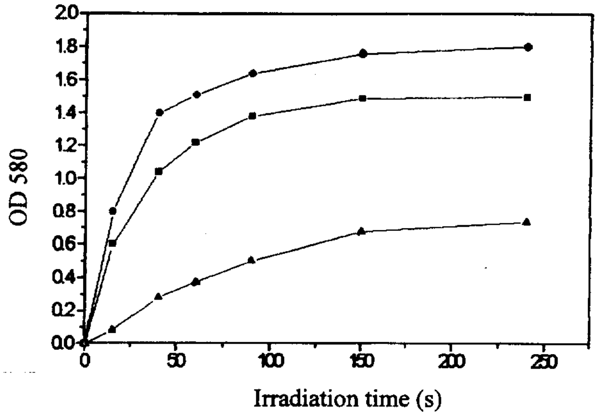


Fig. 6. Effect of counterions of iodonium salt on the photocolour formation; [FR], 10^{-4} M; [onium], 10^{-4} M; ▲, FR/OPPIB; ■, FR/OPPIP; ●, FR/OPPIA.

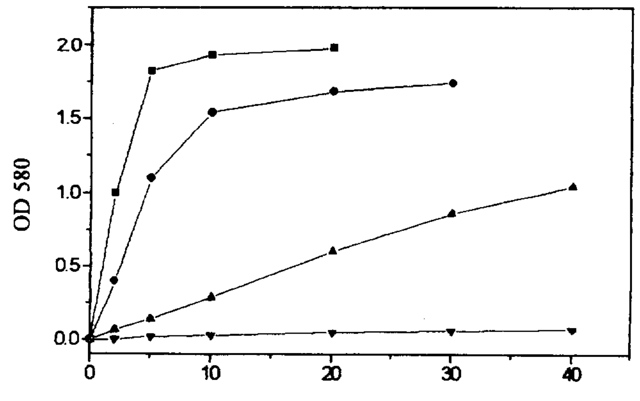


Fig. 7. Effect of OPPIP concentration on the photocolour formation; [FR], 10^{-4} M; acetonitrile; [OPPIP] (M): ▼, 10^{-5}; ▲, 10^{-4}; ●, 10^{-3}; ■, 10^{-2}.

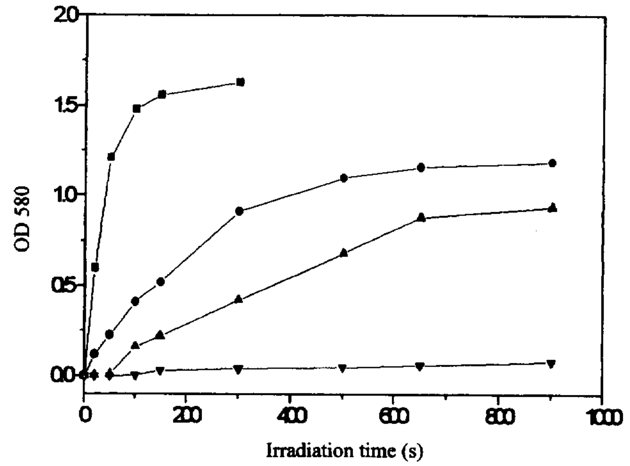


Fig. 8. Effect of FR concentration on the photocolour formation; [OPPIP], 10^{-4} M; [FR] (M): ▼, 10^{-5}; ●, 10^{-4}; ■, 10^{-3}; ▲, 10^{-2}.

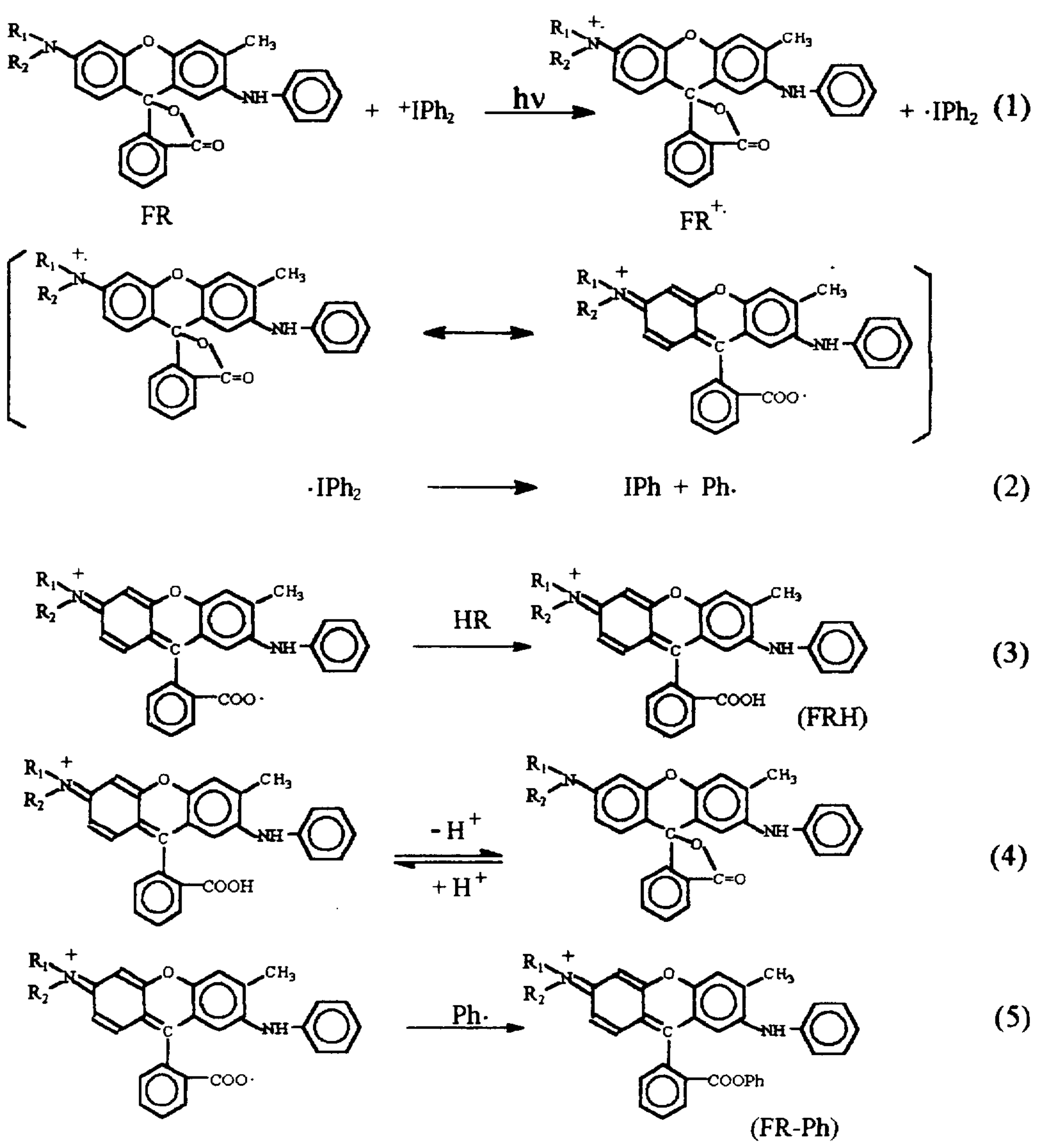
3.2. Mechanism of colour formation

To determine the process of the photoinduced electron transfer colour development reaction, the photoproducts of

Table 2

Volatile products of the photoreaction between FR and DPIOB measured by GC–MS

GC	MS		
Retention time (s)	Content (%)	*m*/*e*	Compound
35	3.2	78	PhH
226	2.9	112	PhCl
434	89.1	204	PhI
961	1.6	154	Ph-Ph
1141	3.1	280	IPh-Ph

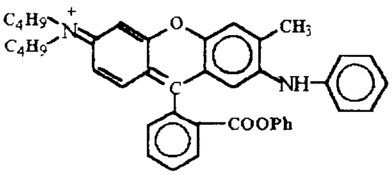


Scheme 1. Photoinduced electron transfer colour formation of FR in the presence of iodonium salt.

FR/DPIOB were analysed. Of these, the volatile products separated and identified by gas chromatography–mass spectrometry (GC–MS) (see Table 2) include iodobenzene (89.1%) and other side-products (e.g. chlorobenzene, phenylbenzene, iodophenylbenzene: total, 10.9%). The latter are formed by the coupling or disproportionation of phenyl radicals, which, together with iodobenzene, can be attributed to the decomposition of the iodonium salt. This is further supported by the photoinduced electron transfer of xanthene dye and iodonium salt [7,8].

As mentioned above, the coloured form of the photoreaction of FR with iodonium salt may be an acidic ring-opened structure. Since this acidic ring-opened coloured form is unstable, the reversible deprotonation reaction easily occurs in the presence of a plasticizer, such as dioctylphthalate or dioctyladipate, non-polar solvents or basic medium [16–18]. In order to demonstrate this, the changes in the optical density were measured on addition of basic triethylamine (TEA) to a black solution of FR/DPIOB. The black colour gradually disappears and the optical density at 580 nm decreases with increasing TEA concentration; however, when the optical density has decreased to 0.09 from 0.78, no more change occurs and the slight black colour remains even at high TEA concentration (10^{-1} M). This indicates that, in addition to the acidic ring-opened coloured form, there may exist another type of stable black form in a small proportion (approximately 10%). Therefore the stable black solid product of FR/DPIOB was separated by chromatography. A reversible colour disappearance occurs rapidly for most of the black solid products in the eluent of ethyl acetate ester and petroleum ether, but a small amount of the purified stable black product was obtained and further identified by MS and IR. Its molecular ion peak (*m*/*e*) was found to be 609, and the $\nu_{C=O}$ absorption band at 1720 cm^{-1} was very different from that of FR lactone at 1743 cm^{-1}. Therefore this stable black product is the same as the product of thermo-colouration of

FR/DPIOB [19]: ring-opened cationic phenyl ester (FR-Ph).



(FR-Ph) M/e: 609

On the basis of the above results, it is reasonable to propose that the process of photoinduced electron transfer colour formation for FR/DPIOB may occur as described in Scheme 1. On irradiation, electron transfer takes place between the excited FR colourless lactone and the DPIOB salt to generate the FR cation radical ($FR^{\cdot +}$) and diphenyliodonium radical ($^{\cdot}IPh_2$); the latter is unstable and decomposes to iodobenzene (PhI) and phenyl radical ($Ph^{\cdot}$) rapidly, and the stable FR cation radical may decay via two different pathways: abstraction of a hydrogen atom from the solvent or other hydrogen donors to form an acidic ring-opened coloured form, or coupling with the phenyl radical to yield the stable coloured ester form (FR-Ph). The coloured forms are mainly derived from the abstraction of hydrogen by the dye radical intermediates and this type of coloured form easily undergoes a reversible colour disappearance reaction in non-polar solvents or basic medium. This decay of the stable dye radical through the abstraction of hydrogen has also been reported in other dye-photosensitized systems [20,21]. In addition, because the coloured form from the coupling of the radicals is very stable, it may be an effective pathway to improve the colour stability on addition of an appropriate radical generator to the colour development system consisting of fluorane and iodonium salt. Further work is in progress.

Acknowledgements

The authors thank the National Science Foundation of China for financial support.

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