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Electron Transfer Coloration of Fluorane Leuco Dyes with Iodonium Salt—an Approach for Color Stabilization

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ABSTRACT

A thermocoloration system consisting of a fluorane leuco dye (FR) and an iodonium salt (DPIOB) was investigated. The color for the FR/DPIOB system possesses a highly colored stability. The rates of the color development reaction show a rapid rise with increase in temperature, and, owing to two kinds of different activation energy (E_a) at the range of reaction temperature in the polymeric film, the reaction easily occurs in the high temperature region (> 104°C). The thermal susceptibility increases with increase of FR/DPIOB content. A mechanism of thermocoloration via *an electron transfer process is proposed. FR is oxidized to the $FR^{+\bullet}$ radical, the iodonium cation is reduced to the diphenyl iodine radical, which then rapidly decomposes to iodobenzene and the phenyl radical. The ring opened cationic ester (FR–Ph) is formed by radical coupling between $FR^{+\bullet}$ and the phenyl radical. © 1998 Elsevier Science Ltd*

Keywords: electron transfer, coloration, stability fluorane, iodonium salt.

INTRODUCTION

Fluorane dyes are important functional dyes which have been widely used as pressure- and heat-sensitive dyes for carbonless papers and facsimile transmission. Due to the different substituents in the fluorane skeleton, various

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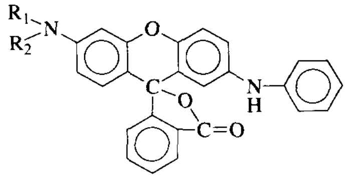
fluorane is a colorless lactone and a proton acceptor, and thus in presence of acidic coreactants (proton donors), normally phenolic compounds [1–2], it can undergo ring opening to form the corresponding highly colored fluorane cation. However, since this acid–base equilibrium reaction is reversible, when the color image makes contact with a plasticer such as dioctylphthatate or dioctyladipate or solvents, especially nonpolar solvents, the reverse deprotonization reaction occurs and the color image fades [3]. In order to increase the color stability, in addition to efforts to synthesize new types of fluorane dyes, many other approaches have been made [4–6]. For example, addition of sensitisers which can liberate a proton and enable reaction to proceed in the forward direction; or addition of zinc or nickel carboxylic complexes which can stabilize the ring opening structure by complexation of amphoteric counter ions; or conversion of the fluorane lactone to the ring opened xanthene ester, which is then oxidized to the coplanar conjugated fluorane cationic ester. Although these methods of adding the additives or changing the structure of the color former can improve the color stability of the fluorane dye, some limitations in these methods still retard their practical application. Because of the presence of the alkylamino substituent in the skeleton the fluorane lactone can also be used as an electron donor, and thus the color development reaction might be readily approached by choosing an appropriate electron acceptor as a developer, through an electron transfer instead of a proton transfer route. Onium salts such as iodonium and sulfonium salts have a low reduction potential and are usually used as electron acceptors in dye sensitized photopolymerization [7–8]. Therefore, on the basis of photoreaction between the xanthene dye and the iodoniumcation, the thermocoloration system comprising colorless fluorane lactone and iodonium salt was investigated and a reaction mechanism proposed.

EXPERIMENTAL

The fluorane leuco dyes (FR-1, FR-2) were supplied by YAMADA Chem. Co. Ltd and purified by recrystallization from benzene. Diphenyliodonium tetrafluoroborate (DPIOB) was synthesized according to the literature.[9] Polymeric films were made from a toluene solution of polymethylmethacrylate (PMMA)/FR/DPIOB and the thickness of film was about 20 µm. The nonvolatile component of the dye moiety was separated by column chromatography using ethyl acetate petroleum ether (5 : 1/v :v) as eluent. Gas chromatography–mass spectrometry analyses were performed on a Finnigan 4012C system. Differential scanning calorimeter (DSC) data was measured on a TA 910S system. Absorption spectra were recorded on a Hitachi 557 UV–Vis spectrophotometer and IR spectra on a Perkin-Elmer 983G.



(FR)

	R_1	R_2
FR-1	n-C_4H_9	n-C_4H_9
FR-2	C_2H_5	i-C_5H_{11}

RESULTS AND DISCUSSION

Color development reaction of FR with DPIOB

FR leuco dye is very stable at room temperature in presence of DPIOB salt, and their solution in various solvents hardly undergoes coloration even after a long time of heating; therefore, the thermal reactivity is low for FR/DPIOB under the condition of low concentration. However. FR/DPIOB thermocoloration was readily observed in polymer film or in the melted state. As shown in Fig. 1 the coloration of FR-1/DPIOB occurs in the PMMA thin film at 137°C. It is clear that two absorption peaks at 440 and 580 nm appear and gradually increase with increase of heating time. Herein it is of importance to point out that the FR colored form possesses high stability and does not fade in the solvents.

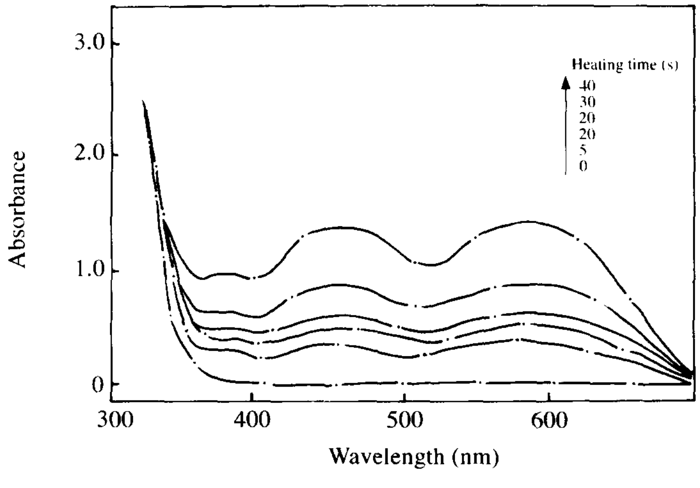


Fig. 1. Changes in the absorption spectra of the FR-1/DPIOB system with heating time at 137°C. [FR-1]: 0.116 mol l^{-1}, [DPIOB]: 0.116 mol l^{-1}.

Because the absorption spectrum of the FR/DPIOB system varies with heating time the thermocoloration reaction can be kinetically monitored by the spectral method. Figure 2 shows the optical density at 580 nm for FR-1 and 582 nm for FR-2 as a function of the heating time at different reaction temperatures. It is of interest to note that the rate of thermocoloration distinctly accelerates in the high temperature region. If the thermocoloration reaction for the FR/DPIOB system follows a second order reaction, i.e. $-dC/dt = k_c[C]^2$, the rate constants (k_c) can be approximately calculated on the basis of Beer's law. From the plot of k_c vs $1/T$ (Fig. 3), it can be seen that the k_c value shows a rapid increase in the lower temperature region compared with that in the higher temperature region. The activation energy (E_a) can also be further deduced according to the Arrhenius equation ($\ln k_c = A - E_a/RT$). At the range of reaction temperature >90°C, there are two different E_a values, 135 kJ mol^{-1} in the low temperature region and 45 kJ mol^{-1} in the high temperature region, and the turning point is about 104°C. This result indicates that the thermocoloration for the FR/DPIOB system occurs much more easily in the higher temperature region above 104°C than that in the region below <104°C. The difference in activation energy is possibly related to the transition temperature (*T*g) of the polymeric medium. Molecular movement is strongly restricted in the glassy state (*T*< *T*g), and thus high activation energy is required at the lower temperature.

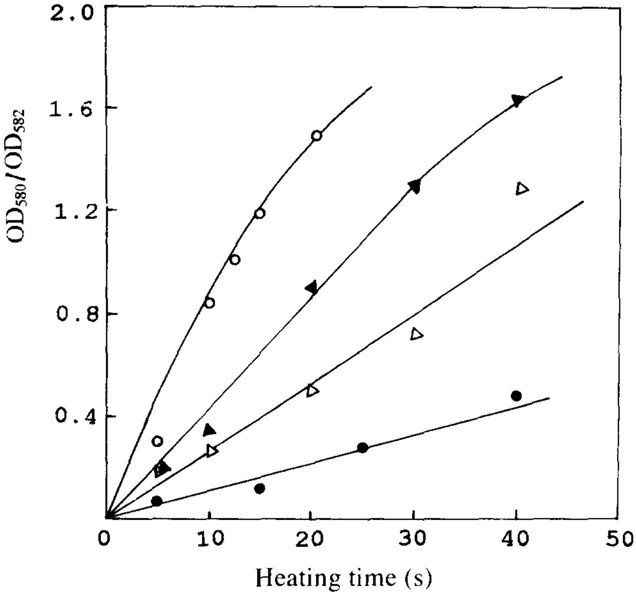


Fig. 2. Changes of optical density at λ_{max} with heating time at different temperature. [FR-1] ; 0.116 mol l^{-1} [FR-1]: 0.116 mol l^{-1}, [DPIOB]:0.116 mol l^{-1}, FR = 1/DPIOB: △ 137°C, ▲ 153°C; FR-2/DPIOB: ● 92°C, ○ 158°C.

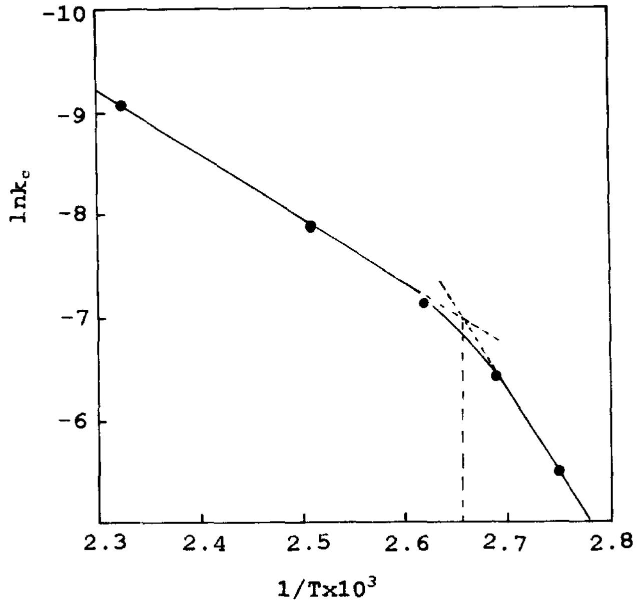


Fig. 3. Plot of rate constant (k_c) vs 1/T for FR-2/DPIOB at different temperatures.

Figure 4 shows the effect of the FR/DPIOB content on the thermocoloration in the film. It is seen that the higher the FR/DPIOB content, the higher is the thermal susceptibility. To obtain highly colored density, it is desirable to have a high concentration of FR/DPIOB in the film. The film containing FR/DPIOB retains good color stability over a range of different optical density. Nevertheless, owing to the limitation of FR/DPIOB solubility in PMMA, excess FR will result in a decrease of the transparency of thin film, and the optimum content is within the range of 5–7%.

Mechanism of thermocoloration for FR in presence of DPIOB salt

Since FR lactone can act as either a proton acceptor or an electron donor, there might exist two different pathways which result in the formation of the FR colored form: i.e. proton transfer or electron transfer. The coloration mechanism as usually proposed includes a protonization of the carbonyl oxygen of the lactone, followed by ring opening to form the highly colored cationic dye. Thus the color formation can possibly be caused by the acidic products directly generated from the thermal decomposition of the DPIOB salt. The result obtained by differential scanning calorimeter (DSC), as shown in Fig. 5, demonstrates that only one peak appears at the melting point 140°C of DPIOB, even when the heating temperature approaches 200°C. Obviously, it is unlikely that the thermo-coloration for the FR lactone can undergo the route of proton transfer with the DPIOB salt under the experimental conditions.

To establish the possible mechanism, the products of the thermal reaction were analyzed by GC–MS. The results reveal that the volatile products upon heating are iodobenzene (86.6%) and other side products, including benzene

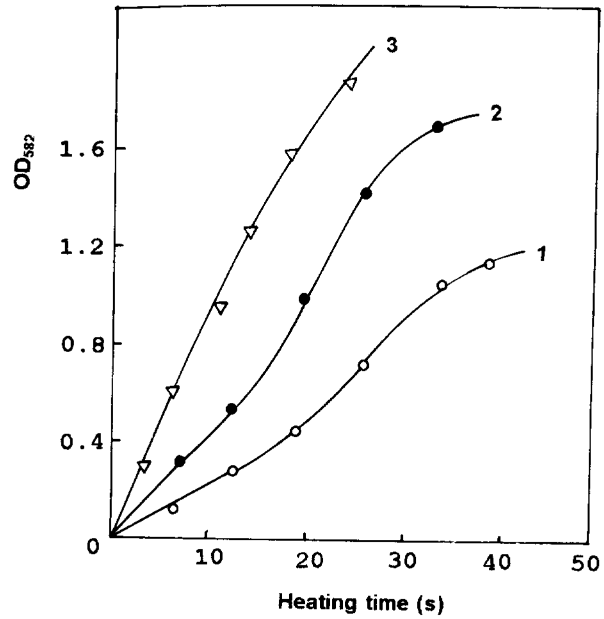


Fig. 4. Curves of optical density at λ_{max} vs heating time with different FR-2/DPIOB content at 137°C. FR-2/DPIOB(1 : 1), (wt%): (1)3%; (2)5.0%; (3)7%.

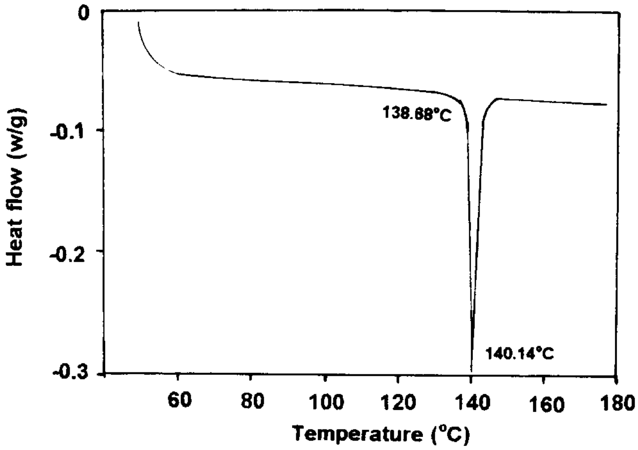
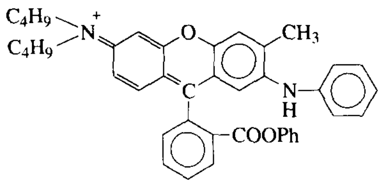


Fig. 5. DSC curve of diphenyliodonium salt.

phenylbenzene, chlorobenzene, iodophenylbenzene etc., (totally 13.4%), which are formed by coupling or disproportionation of phenyl radicals. According to the mechanism of the photoinduced electron transfer of xanthene dye with iodonium salts [8], iodobenzene and the phenyl radical are generated by the decomposition of the iodonium radical intermediate. In view of the fact that the proportion of iodobenzene is much higher than that of the phenyl radical products, it seems that most of phenyl radical might combine with the FR moiety, or others.

The nonvolatile products were further separated by column chromatography. A stable black solid thus obtained was measured by MS and its molecular ion peak (M/e) was found to be 609. Additionally, a remarkable change in the $V_{C=O}$ absorption band from 1743 cm^{-1} (lactone) to 1720 cm^{-1} (ester) was observed. Therefore, the black product of the thermocoloration is suggested to be the ring opened cationic phenyl ester (FR–Ph):



(FH-Ph) M/e: 609

In order to further show the difference in color stability between the FR/DPIOB system and the usual acid color development system, e.g. FR/BPA (bisphenol A) system, comparisons were carried out in the experiment. As shown in Tables 1 and 2, when the black products obtained were reheated to the melted state or dissolved in a solvent (e.g. alcohol, acetonitrile. 1,4-dioxan, chloroform, etc.), the black disappears rapidly for the FR/BPA system, but it is very stable for FR/BPIOB. This implies that the acidic color form is not stable due to its reversible reaction, whereas the esteric color form (FR–Ph) is stable and irreversible.

TABLE 1
Volatile Products of Thermocoloration for FR/DPIOB At 137°C

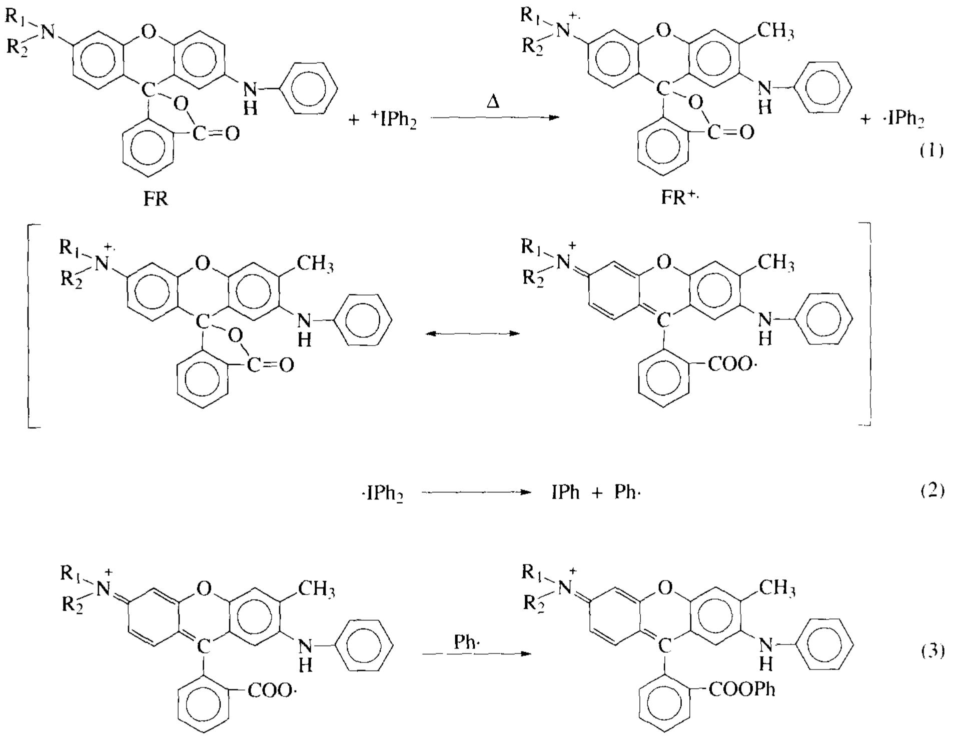
GC		*MS*	
Retention time (s)	*Content (%)*	*M/e*	*Compound*
29	1.7	78	PhH
43	6.4	45, 59, 72	
147	1.2	112	PhCl
408	86.6	204	PhI
920	3.0	154	Ph–Ph
1239	0.9	280	IPh–Ph

TABLE 2
Comparison of Color Stability for FR/BPA and FR/DPIOB Systems

System	*Heating*	*Melted state*	*Solvent*
FR/BPA	+	–	–
FR/DPIOB	+	+	+

+ black; – black disappearance.

Based on the above results, it is reasonable to propose that the thermo induced coloration or FR/DPIOB predominantly occurs through the electron transfer process, as shown in Scheme 1. In the reaction temperature range, the FR colorless lactone and the DPIOB salt undergo redox reaction to generate the FR cationic radical and the diphenyliodine radical, which is unstable and rapidly decomposes to iodobenzene and the phenyl radical; then FR cationic radical then couples with the phenyl radical to yield the stable colored ester form (FR–Ph). The proposal of this electron transfer mechanism may be an effective approach to obtain stable colored form pro-



Scheme 1

ducts from lactone type colorless precursors, when used in combination with an appropriate electron accepter as a developer.

ACKNOWLEDGEMENT

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