Film device to visualize UV irradiation

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Abstract

A film device to visualize UV irradiation was successfully fabricated by an agarose solid film containing Fluoran dye, acid generator *N*-tosyloxyphthalimide and 2-propanol medium, and the mechanism and kinetics of this system were investigated. The reactions involving: (1) acid generation from *N*-tosyloxyphthalimide by UV irradiation, (2) acid generation from *N*-tosyloxyphthalimide by chemical amplitude reaction, (3) coloring reaction of Fluoran dye by acid were analyzed by changing the Fluoran dye concentration. The concentration of the colored Fluoran dye was determined by the absorbance at 520 nm appearing by UV irradiation. The kinetic constants of the three reactions were estimated by solving the differential equations by the formation of the colored Fluoran dye with changing the parameters based on a least square method. The result was in accordance with the experimental results to give reaction rate constants of the processes.
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1. Introduction

Detection of harmful electromagnetic irradiation such as UV light and gamma ray is of importance. There are various methods for detecting such electromagnetic waves. It is preferable to visualize the degree of exposure to harmful electromagnetic waves in order to detect in situ. Coloring materials have been used for visualization devices of gamma ray, such as azo-base dye [1], polyvinyl chloride containing a dye [2], etc. but the sensitivity of these devices has been low.

Highly sensitive visualization devices of gamma and UV rays have been studied in an alcohol solution containing dye and acid generating material. One example is a 2-propanol solution containing Fluoran dye as coloring material and *N*-tosyloxyphthalimide as acid generator [3,4]. However, it has been difficult to use this system as a solid device since the reaction requires the presence of medium (alcohol in this case). We have attempted to make a solid device from the system of Fluoran dye and *N*-tosyloxyphthalimide by adsorbing them onto a cellulose paper, cellulose powders, silica gels, and Vycor Glass (porous glass), but these solid systems were insensitive to electromagnetic irradiation.

Recently, we found that chemical reactions can take place in a solid composed of a polysaccharide and excess water the same as in an aqueous solution [5]. This solid involves nanoheterogeneous three-dimensional network structure composed of main chain of the polysaccharide. This solid can be formed as a film suitable for fabricating devices. Since the presence of water induces coloration of the Fluoran dye and *N*-tosyloxyphthalimide system, the water in the solid was replaced by 2-propanol solvent, and thereafter Fluoran dye and *N*-tosyloxyphthalimide were adsorbed from their 2-propanol solution into the solid, which successfully produced a sensitive film to detect UV irradiation by coloration [5]. Since the details of the coloring reaction of the solid device have not been analyzed yet, they are reported in this paper.

2. Experimental

2.1. Materials

Fluoran dye (3′-methoxy-6′-diethylamino-spiro[isobenzofuran-1(3H),9′-[9H]xanthene]-3-one) (**1**, FL) was obtained from Yamada Chem. Co. Ltd. and purified by recrystallization from chloroform. *N*-tosyloxyphthalimide (**2**,

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TOPI) was prepared by the literature method [6–8], and agarose pure powder (**3**) was obtained from Acros Organics. The purest grade 2-propanol was obtained from Kishida Chemical Co., Ltd. and dehydrated over molecular sieve 3A before use.

1.Fluoran dye (FL)

2. N-tosyloxyphthalimide (TOPI)
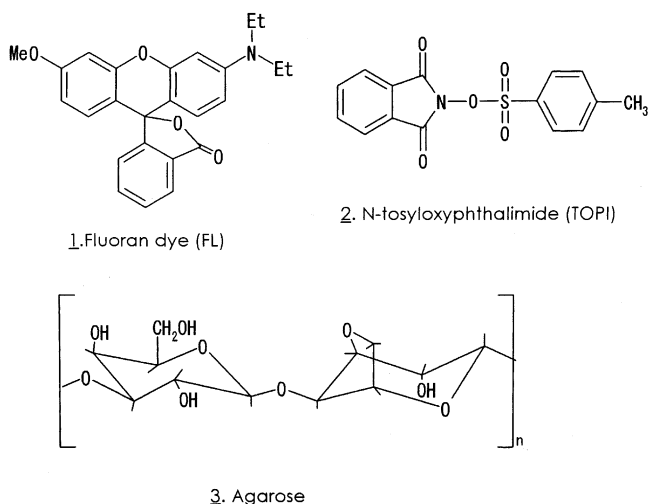
3. Agarose

2.2. Preparation of agarose solid film

Two weight percent agarose powders were put into pure water and heated by irradiating very carefully a high frequency wave (2.54 GHz) in an electric oven to entirely solubilize the material. A hot agarose solution was poured into a mold (20 mm × 9 mm × 2 mm size) made of glass. After cooling the clear solution to room temperature under ambient conditions, a tight, and elastic solid film was obtained. The solid was a little bit turbid because of the agarose network structure.

A 2 wt.% agarose solid involving excess water was freeze-dried to prepare a material involving no water, and the scanning electron microscope (SEM) was measured for the dry sample.

In order to exchange water in the agarose solid film by 2-propanol, the film (containing excess water) was placed in a dry 2-propanol (about 20 ml), and the water was exchanged by 2-propanol four times during 4 days. After completely exchanging the water by 2-propanol in the agarose solid film, the film became 18 mm × 8 mm × 1.8 mm size.

A 2-propanol solution of TOPI and FL was adsorbed into the agarose film containing excess 2-propanol. For this purpose the 2-propanol solution of FL (3.0×10^{-4} mol dm^{-3}) and TOPI (0.0 to 3.0×10^{-3} mol dm^{-3}) was used. The concentrations of the TOPI and FL in the film were determined by visible absorption spectrum with a Shimadzu Multispec-1500 spectrophotometer as mentioned in Section 3.

2.3. Irradiation by UV light

The agarose film containing the 2-propanol solution of TOPI and FL was put into a quartz cell filled with 2-propanol vapor, and irradiated with a mercury lamp (SEN Lights Corp. Handy cureruv HLR100T-1) through a UV bandpass filter (Asahi Techno Glass Corp. UV-D33S) at room temperature (25 °C) with the irradiation intensity of 142 mW cm^{-2}. The concentration of the colored FL was determined by the absorption maximum at 520 nm ($\varepsilon = 4.0 \times 10^4$ mol^{-1} dm^3 cm^{-1}) by the visible absorption spectrum.

For the reference experiment in a homogeneous solution, a cell with the same size of the solid (18 mm × 8 mm × 1.8 mm size) was prepared by glass and irradiation on the 2-propanol solution involving the same concentration of FL and TOPI was carried out under the same experimental conditions as the solid film system.

3. Results and discussion

The SEM of the freeze-dried agarose solid is shown in Fig. 1. It shows at least μm order network of the agarose chains. Although smaller dimension of structure less than 100 nm cannot be seen in this picture, such network works to form a solid state film involving a large amount of liquid. The hardness of the 2 wt.% agarose solid containing water was the same as a brick cheese and one third of a conventional laboratory rubber stopper.

The adsorbed concentration of FL and TOPI were determined by the differential spectra (Fig. 2C) obtained from the spectra before (Fig. 2B) and after (Fig. 2A) adsorption of the solution into the agarose film. The concentrations of FL and TOPI were obtained by using the absorbance at 296 and 311 nm of the differential spectra (Fig. 2C) and molar absorptivity of FL (ε (296 nm) $= 1.05 \times 10^4$ mol^{-1} dm^3 cm^{-1}, ε (311 nm) $= 7.78 \times 10^3$ mol^{-1} dm^3 cm^{-1}) and TOPI (ε (296 nm) $= 1.87 \times 10^3$ mol^{-1} dm^3 cm^{-1}, ε (311 nm) $= 6.18 \times 10^2$ mol^{-1} dm^3 cm^{-1}). The 2-propanol in the film could well be exchanged by the 2-propanol solution of FL and TOPI. The concentrations of the adsorbed FL and TOPI in the agarose film were thus determined (vide infra) and it was confirmed that the adsorption was finished in about 30 min, so that throughout the experiments the adsorption time was fixed to 30 min.

The adsorption of FL and TOPI into the agarose film, i.e. exchange of the pure 2-propanol in the solid by the solution, as a function of their concentration in the original (before exchange) solution is shown in Fig. 3, where the initial concentration of FL was fixed to 3.0×10^{-4} mol dm^{-3} and that of TOPI was changed from 0.0 to 3.0×10^{-3} mol dm^{-3}. The concentration of the adsorbed FL was almost constant and that of TOPI was almost proportional to the initial concentration. Various samples with different solution concentrations were prepared as Fig. 3 and Table 1.

Table 1
Adsorbed concentration of FL and TOPI into the agarose film

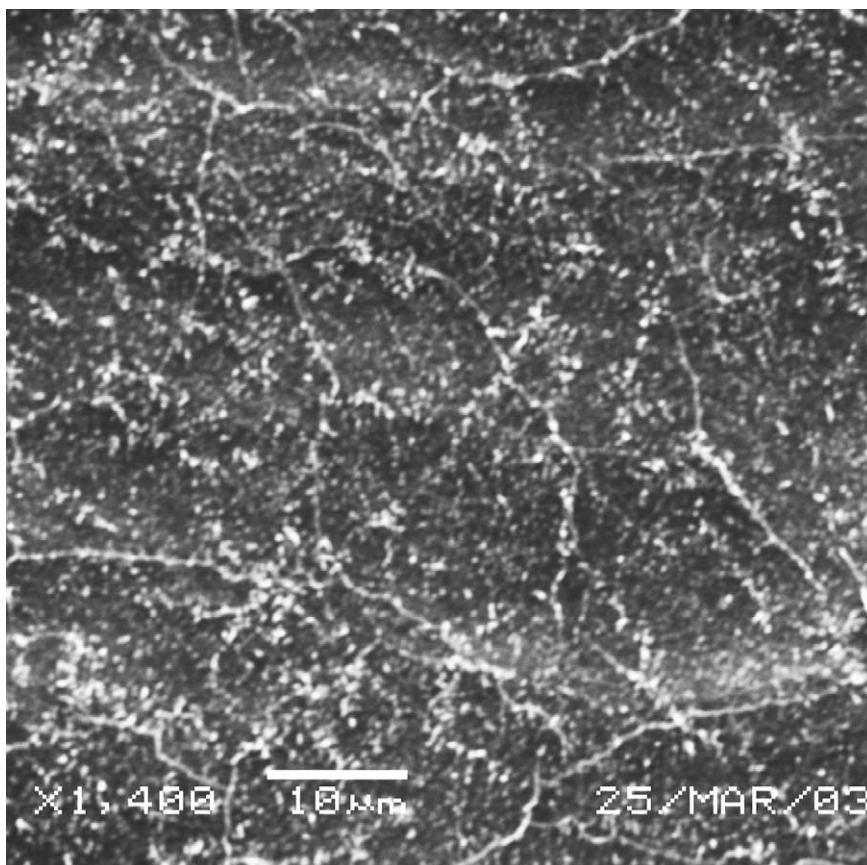| FL (10^{-3} mol dm^{-3})	0.14	0.12	0.18	0.13	0.12
TOPI (10^{-3} mol dm^{-3})	0.00	0.40	0.52	0.86	1.92

Fig. 1. Structure of freeze-dried agarose solid film as studied by SEM.
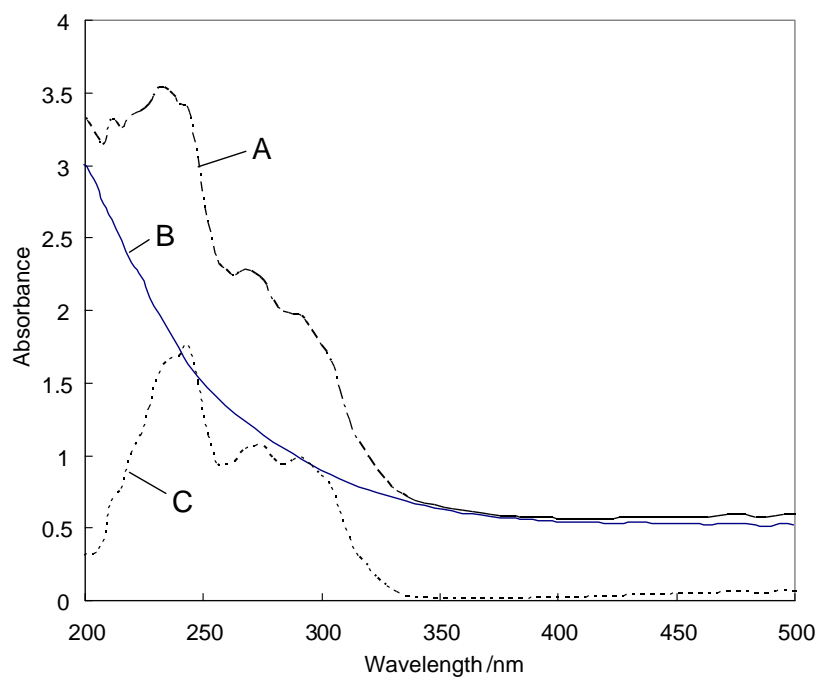

Fig. 2. UV/Vis absorption spectra of FL and TOPI in agarose film: (A) after adsorption and (B) before adsorption of the solution (FL, 3.0×10^{-4} mol dm^{-3} and TOPI, 3.0×10^{-3} mol dm^{-3}) into the film, (C) differential spectrum of A and B.
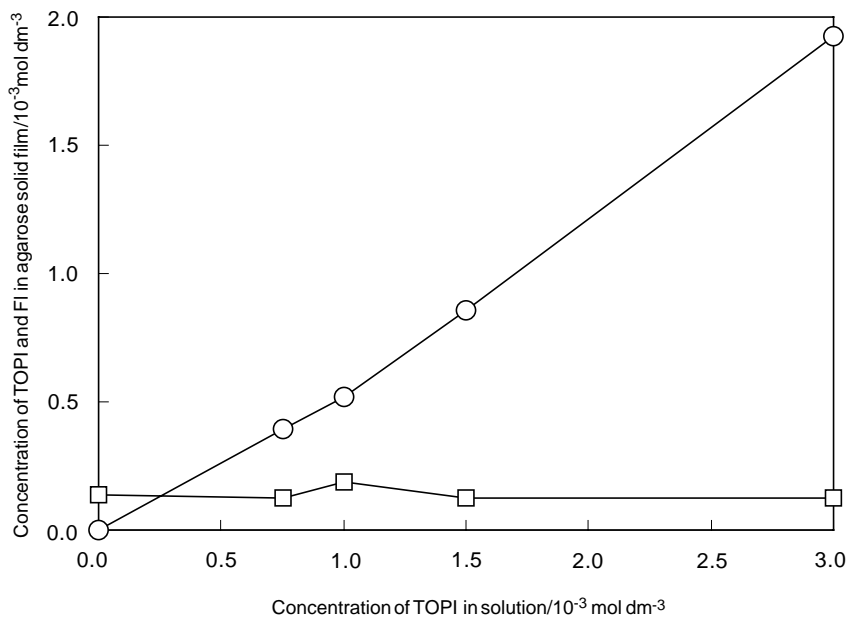
Fig. 3. Adsorbed concentrations of TOPI and FL in agarose solid film: (○) TOPI; (□) FL. FL concentration in solution for adsorption is 3.0×10^{-4} mol dm^{-3}.

The absorption spectral change of the agarose film containing the 2-propanol solution of FL and TOPI by UV irradiation is shown in Fig. 4. A rapid increase in the absorption at $\lambda_{max} = 520$ nm was observed as the result of the formation of colored FL (FLc) species. From these data, the FLc concentrations were obtained against irradiation time, and shown in Fig. 5.

[9]. Moreover, the diffusion coefficient (D_{app}) of the solute in the agarose or κ-carrageenan solid is close to the value in a solution ($D_{app} = 10^{-5}$ to 10^{-6} cm^2 s^{-1}) [9]. The reaction mechanism in the present solid can be represented by the following reactions [3,4,6] the same as in a homogeneous solution.

$$(1)$$
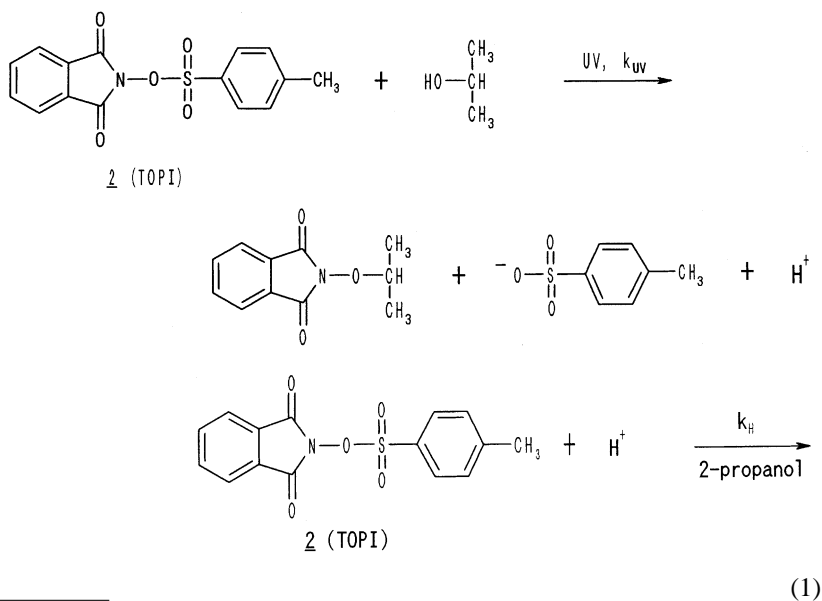
As the reference experiment, the result of UV irradiation on the 2-propanol solution ($[FL]_0 = 0.12 \times 10^{-3}$ mol dm^{-3}, $[TOPI]_0 = 1.9 \times 10^{-3}$ mol dm^{-3}, cell size $= 18$ mm $\times$ 8 mm $\times$ 1.8 mm) is shown in Fig. 6.

We have reported that the electron transfer from the photoexcited Ru(bpy)$_3^{2+}$ to MV^{2+} in the agarose or κ-carrageenan solid takes place the same as in a solution
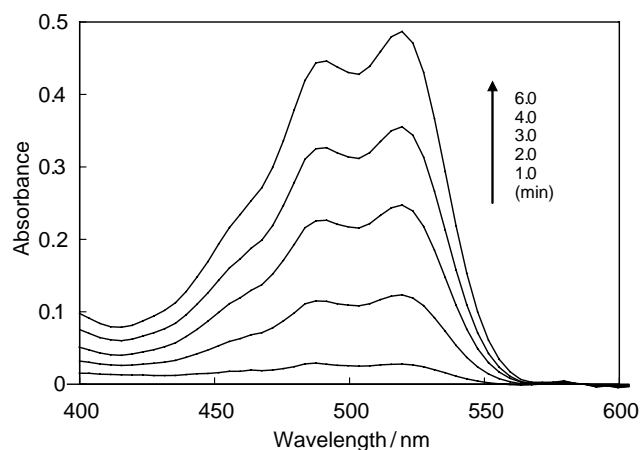

$$(2)$$
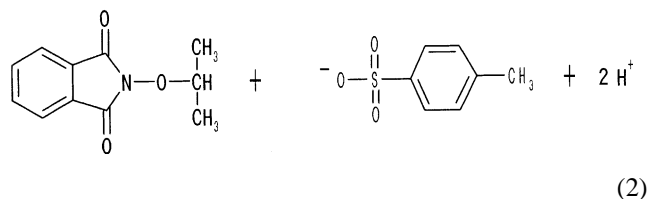
Fig. 4. Spectral change on UV irradiation. $[FL]_0: 1.23 \times 10^{-4} \, mol \, dm^{-3}$; $[TOPI]_0: 1.92 \times 10^{-3} \, mol \, dm^{-3}$.
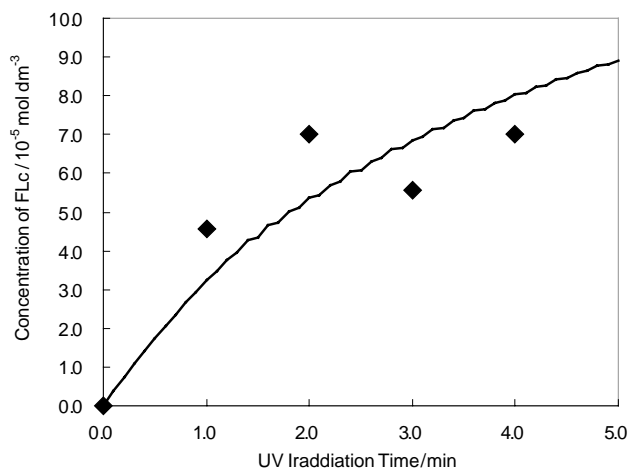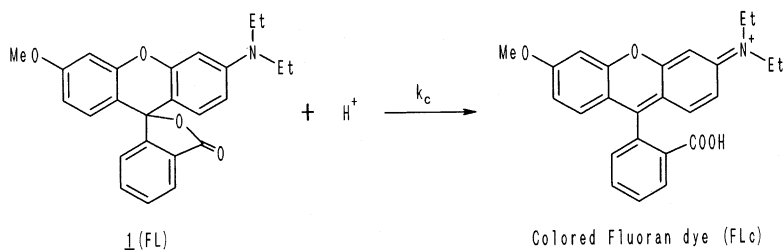

Fig. 6. Irradiation time vs. [FLc] in solution. $[TOPI]_0: 1.9 \times 10^{-3} \, mol \, dm^{-3}$; $[FL]_0: 0.12 \times 10^{-3} \, mol \, dm^{-3}$. The curve is a stimulated one.

$$(3)$$

k_{UV} is the pseudo-1st order rate constant of proton generation from TOPI by UV light irradiation; k_H the 2nd order rate constant of proton generation by chemical amplitude reaction of TOPI; k_C the 2nd order rate constant of coloring reaction of FL by proton.

Eq. (1) shows proton generation from TOPI by UV irradiation. Eq. (2) shows chemically amplified reaction of proton generation from TOPI in which the p-methylbenzenesulfonic acid dissociates to liberate the second proton. Eq. (3) represents coloring reaction of FL by the liberated proton.
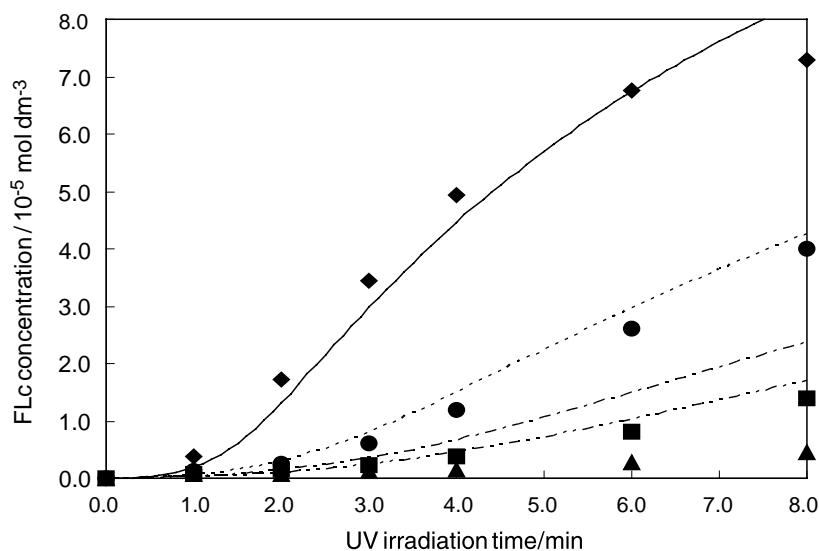

Fig. 5. Irradiation time vs. [FLc] in solid films. $[TOPI]_0$: (◆) $1.9 \times 10^{-3} \, mol \, dm^{-3}$; (●) $8.6 \times 10^{-4} \, mol \, dm^{-3}$; (■) $5.2 \times 10^{-4} \, mol \, dm^{-3}$; (▲) $4.0 \times 10^{-4} \, mol \, dm^{-3}$. The curve lines are simulated ones (for TOPI: (—) $1.9 \times 10^{-3} \, mol \, dm^{-3}$; (- - -) $8.6 \times 10^{-4} \, mol \, dm^{-3}$; (- · ·) $5.2 \times 10^{-4} \, mol \, dm^{-3}$; (- · · -), $4.0 \times 10^{-4} \, mol \, dm^{-3}$), so that the deviation from all the experimental points become minimum. $[FL]_0: 1.23 \times 10^{-4} \, mol \, dm^{-3}$.

On the basis of these equations, we analyzed the coloring reactions by the following equations:

$$\frac{d[H^+]}{dt} = k_{UV}[TOPI] + k_H[TOPI][H^+] - k_C[FL][H^+] \quad (4)$$

$$\frac{d[FLc]}{dt} = k_C[FL][H^+] \quad (5)$$

The proton concentration of the system at a certain time is determined by Eq. (4), and FLc concentration by Eq. (5) for which FLc concentration is determined from the absorption spectra of Fig. 4. Since it was difficult to determine exactly the TOPI concentration from the absorption spectrum during the reaction, it was determined by simulation. On the basis of Eqs. (4) and (5), we simulated the increase of the FLc concentration in the film. The method of calculation is as follows:

(1) At $t = 0$, initial concentrations of TOPI and FL are shown in Fig. 3 and Table 1. It was assumed that 100% TOPI (absorbance at 296 nm is 0.66 for the 1.8 mm light path length) is excited and reacts with 2-propanol in competition with deactivation of the excited state.
(2) At $t = 0$, initial concentration of H^+ should be nearly zero, because no FLc is present before UV irradiation.
(3) At $t = t_1$ the FLc concentration is shown in Fig. 5.
(4) In Eq. (4), certain values of the rate constants (k_{UV}, k_H, k_C) were assumed, and then $[H^+]$ and $[FLc]$ formed in a small time (Δt) were calculated by Eqs. (4) and (5) to compare the simulated $[FLc]$ with the experimental results.
(5) Such procedures were repeated for the whole reaction time range, and the simulated $[FLc]$ values were compared with the experimental data to obtain best fit rate constants (k_{UV}, k_H, k_C) by the least square method, so that the deviation from all the experimental points become minimum.

The parameters were estimated and are shown in Table 2 both for the solid and solution systems. In Fig. 5 (in solid film) and Fig. 6 (in solution), the best simulated curves are shown for the parameters in Table 2. The k_{UV} value is much smaller than those of k_H and k_C both in the solid and in the solution. The much smaller value of k_{UV} in the solid than in the solution is ascribable to the scattering of the incident light

Table 2
Simulated kinetic constants

Rate constant	In solid	In solution
k_{UV}/min^{-1}	8.2×10^{-2}	1.0×10^1
$(mol^{-1} dm^3 min^{-1})^a$	(6.3×10^{-3})	(7.7×10^{-1})
k_H	1.3×10^3	8.0×10^3
k_C	9.1×10^1	1.6×10^2

[a] Second order rate constant based on [2-propanol] = 13.0 mol dm^{-3}.

by the solid. However, this step affected only the induction period of the FLc formation (refer Figs. 5 and 6) and the FLc concentration formed after longer reaction time (e.g., after 4 min) was not much affected. In the present solid although small molecules and ions can diffuse the same as in a pure liquid, the apparent diffusion coefficient of the FL in the agarose solid film was smaller by five times than in a liquid [5]. The smaller k_H value in the solid film than in the solution (1/6.2) would be ascribable to the diffusion factor of the solute. The reaction (3) (k_C) was not affected much in the solid compared with that in the solution.

Acknowledgements

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