Photochromism of 2-Hydroxytriphenylmethanol and Its Derivatives

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2-Hydroxytriphenylmethanol (HM) shows photochromism in air-saturated acetonitrile and other solvents and also in the crystalline state. The colored form has been deduced to be *o*-fuchsone, produced by photochemical dehydration of HM. The photochromism mechanism is entirely different from that of other triarylmethane derivatives. The colored form is the same species as in thermochromism. The reactive state of HM was found to be the excited singlet state from the results of quenching experiments. The quantum yield of the photochemical reaction was determined to be 0.62 in acetonitrile by a method based on the equilibrium between the photochemical and thermal bleaching reactions. Photochromism occurs also at 77 K. At this temperature, HM radical is produced beside the colored form. The ratio of the concentration of HM radical to the colored form increases with irradiation time. Several HM derivatives show photochromism similar to HM.

Photochromism of many triarylmethane derivatives, especially triphenylmethane derivatives, has been studied extensively.[1] In the photochromism of triarylmethane dye leuco derivatives, such as leuco malachite green and leuco crystal violet, the colored forms are the respective cations.[2,3] In the photochromism of *o*-nitrotoluene derivatives, for example 2,4,2′,4′,2″,4″-hexanitrotriphenylmethane, the colored form is an aci-nitro acid or an anion.[4,5] It has been reported that 2-hydroxytriphenylmethanol[6,7] (HM) and (3-hydroxy-2-naphthyl)-diphenylmethanol[7] show thermochromism. Gomberg and Nishida[6] attributed the thermochromism of HM to the formation of the quinoidal colored form(I), but, Bowden and Beynon[7] suggested the same phenomenon was due to the broadening of the near ultraviolet absorption band. However, both these views do not seem to be fully supported by experimental evidence.

We have found photochromism of HM and its derivatives. The photochromism was studied in various solvents at room temperature as well as at liquid nitrogen temperature. For comparison thermochromism was also studied.

Experimental

Materials. HM was synthesized from methyl salicylate or phenyl salicylate and phenylmagnesium bromide by the Grignard reaction[8] and, after treatment with activated charcoal, recrystallized several times from an ethyl ether–*n*-hexane mixture. 2-Hydroxy-4-methoxytriphenylmethanol (HMM) was also synthesized from 2-hydroxy-4-methoxybenzophenone by the Grignard reaction and, after treatment with activated charcoal, recrystallized several times from ethyl ether–*n*-hexane and methanol–water mixtures. 5-Chloro-2-hydroxytriphenylmethanol and (3-hydroxy-2-naphthyl)-diphenylmethanol were synthesized from 5-chloro-2-hydroxybenzophenone and methyl 3-hydroxy-2-naphthoate by the Grignard reaction and purified by the method used for HM. *o*-Naphthofuchsone was obtained by refluxing dichlorodiphenylmethane, *β*-naphthol and aluminum chloride in carbon disulfide, decomposing the products by ice, steam distilling, and recrystallizing from acetic acid.[9]

Acetonitrile was distilled over phosphorus pentoxide. Ethyl ether was distilled over sodium wire after being stood overnight with calcium chloride and used immediately. Wako G.R. grade acetic acid, methanol and ethanol were used as received.

Piperylene was distilled over sodium wire. Biacetyl was used immediately after distillating three times.

Apparatus. A 6W germicidal lamp was used as a 253.7 nm light source. A Toshiba SHL-100 UV high pressure mercury lamp combined with a Toshiba UV-D2 filter was used for the 365 nm source. An Ushio USH-100 superhigh pressure mercury lamp combined with a photographic plate as a filter was used for the experiment at 77 K. A combination of an Ushio UXL-150 xenon lamp and a Hitachi G-3 grating monochromator was used to obtain 280 nm light for the piperylene quenching experiments.

The absorption spectrum and thermal decay were recorded on a Hitachi EPS-3T spectrophotometer at room temperature. The absorption spectrum at 77 K was measured with a Hitachi 356 Dual-Wavelength spectrophotometer. A JEOL Type P-10 ESR spectrometer was used for measurement of the ESR spectrum.

Results and Discussion

Irradiation of the air-saturated solution of HM in acetonitrile by 253.7 nm light at room temperature turned the colorless solution to a yellowish brown. Photochromism occurs in ethyl ether, 1,2-dichloro-

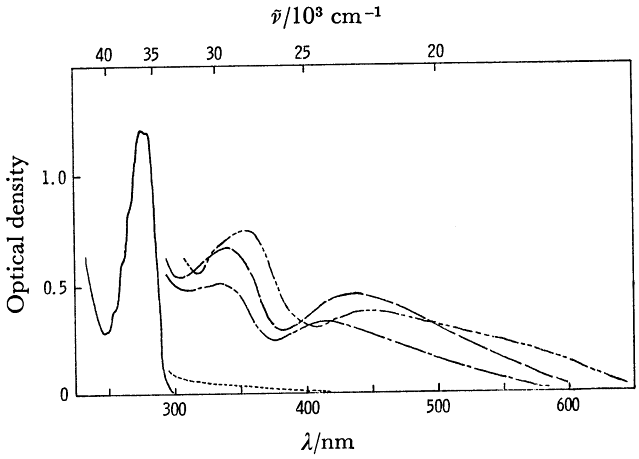


Fig. 1. Absorption spectra of (——) HM in acetonitrile (5.30×10^{-4}M), (-----) the colored form in photochromism of HM in acetonitrile, (—·—) the colored form in photochromism in ethyl ether, and (······) *ca.* 24 hours aged after the irradiation in acetonitrile ceased. Absorption spectrum of (—·-—) the colored form for thermochromism in acetic acid.

ethane, and benzene and also in the crystalline state. The color bleaches gradually and finally disappears on keeping the solution in the dark. The bleaching, however, is not complete. The absorption spectrum after prolonged storage in the dark indicates the presence of a small amount of the irreversible photoproduct as shown in Fig. 1. The absorption spectra of HM in acetonitrile and its colored form in acetonitrile and ethyl ether are also given in Fig. 1. The absorption maxima of the colored form at 340 (A band) and 440 nm (B band) in acetonitrile shift to 334 and 416 nm respectively in the less polar ethyl ether.

The thermochromic colored form in acetic acid has absorption maxima at 354 and 450 nm. The spectrum closely resembles that of the photochromic colored form as shown in Fig. 1.

The photochromic behavior of HMM in polar solvents is similar to that of HM. In contrast to HM, HMM is photochromic at room temperature in saturated hydrocarbons (*n*-hexane, cyclohexane, methylcyclohexane) in which HM merely decomposes photochemically. Furthermore, thermochromism of HMM was observed in *n*-hexane. Hence, comparison of the absorption spectra of the photochromic and thermochromic forms in the same solvent became possible. As seen from Fig. 2, complete agreement was found between the absorption spectra of the photochromic and thermochromic forms. Consequently, it may safely be concluded that the photochromic form is the same species as the thermochromic one.

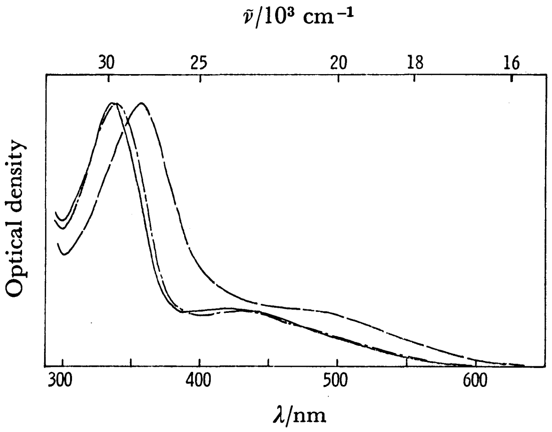


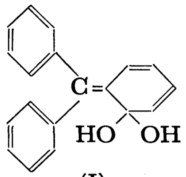
Fig. 2. Absorption spectra (maximum peaks at shorter wavelengths are normalized) of (——) the colorled form in photochromism and thermochromism of HMM in *n*-hexane, (——) the colored form in photochromism of HMM in acetonitrile, and (----) the colored form in thermochromism of HMM in acetic acid.

The rate of bleaching measured for the A band agreed well with that for the B band. The ratio of the optical density of the A band to that of the B band is little affected by solvent and temperature. These observations strongly support the view that both A and B bands originate from the same species and the colored form in photochromism as well as in thermochromism consists of a single species.

The absorption spectra of the colored form of HMM are shown in Fig. 2. The absorption maxima shifted to longer wavelengths when the solvent was changed from ethyl ether to acetonitrile. In acetic acid, the absorption maxima were located at considerably longer wavelengths than in acetonitrile in spite of the smaller dielectric constant of acetic acid. This implies the existence of a specific interaction between solute and solvent. The most plausible one is hydrogen bond formation.

2-Hydroxytriphenylmethyl cation is not the colored form, since its absorption spectrum has maxima at 410 and 438 nm. The radical, which is produced frequently in the photochemistry of triphenylmethane derivatives, may also be excluded because the colored form in acetic acid does not give an ESR signal.

Compound (I) may be considered as a possible structure of the colored form. However, 2-methoxytriphenylmethanol shows neither photochrmism nor thermochromism indicating that the 2-hydroxy group plays an important role. Therefore, (I) may be excluded.



(I)

The thermal bleaching reaction of the colored form of HM obeys first-order kinetics. In acetonitrile the bleaching rate constant is proportional to the concentration of water added, whereas the rate constant is little affected by the addition of *n*-hexane. Similar effects of water and *n*-hexane were observed in ethyl ether solution. The result in acetonitrile is shown in Fig. 3. Thus the first-order kinetics observed in acetonitrile and ethyl ether must be pseudo-first order due to the presence of water as an impurity. In dimethoxyethane, which was so carefully dried over sodium-potassium alloy that the solvent became blue in color due to solvated electrons, the order of the bleaching reaction was found to be close to two. Also, it has been reported that HM dehydrates and then forms 9-phenylxanthene at elevated temperatures.[6] Thus it

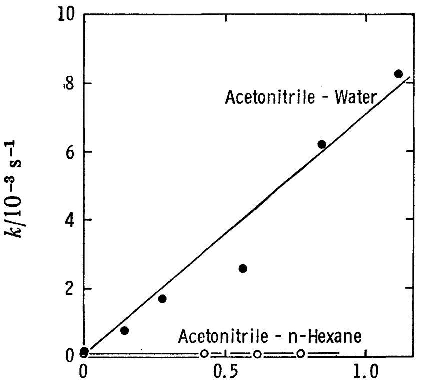
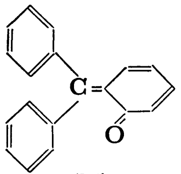
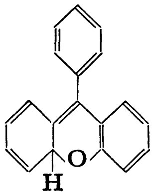


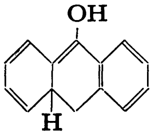
Fig. 3. Effect of added water (●) and *n*-hexane (○) on the first-order bleaching rate constant in acetonitrile.

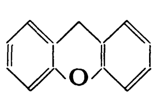
is evident that the colored form is a dehydrated form of HM.

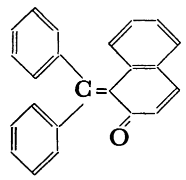
Compounds (II) and (III) are the possible dehydrated forms of HM. In 2-propanol the absorption spectrum of (III′) which has some similarities to (III) in its structure has a maximum at 383 nm,[10] considerably to the blue of the peak for the colored form. The large red shift of the absorption spectrum in acetic acid is not expected for (III). A related compound to (III), xanthene (III″) has absorption maxima at 283 nm and shoulders at 287 and 291 nm in both acetonitrile and acetic acid.


(II)


(III)


(III′)


xanthene
(III″)


o-naphthofuchsone
(IV)

If the colored form is (II), *o*-fuchsone, the observed large red shift in acetic acid can be explained by hydrogen bond formation between (II) and acetic acid. *o*-Naphthofuchsone (IV) is a condensed homologue of *o*-fuchsone, and is stable to be isolated. The absorption spectra of (IV) in two solvents are presented in Fig. 4. The absorption maximum at 360 nm in acetonitrile shifts to 370 nm in acetic acid reflecting the hydrogen bonding with the acetic acid.

Although the colored form can not be isolated for structural determination, spectral and kinetic behavior strongly supports reaction scheme (1) for photochromism as well as thermochromism.

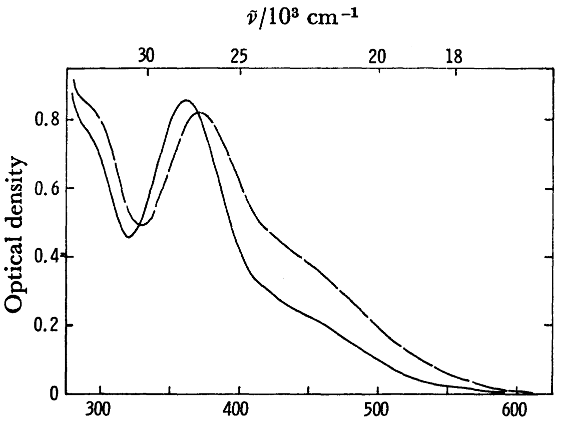
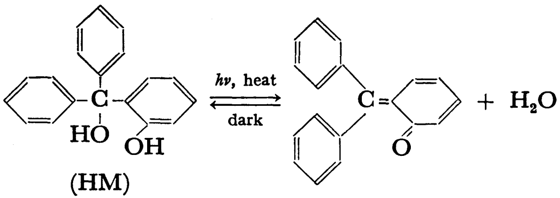


Fig. 4. Absorption spectra of *o*-naphthofuchsone (——) in acetonitrile (1.0×10^{-4}M) and (----) in acetic acid (1.04×10^{-4}M).



(HM)

o-fuchsone
(F)

Scheme 1.

This is a new reaction mechanism for photochromism and thermochromism of triarylmethane derivatives.

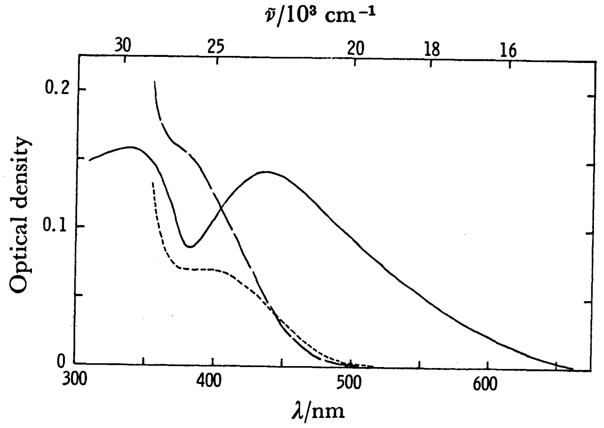


Fig. 5. Absorption spectra of (——) the colored form of ClHM in acetonitrile, (----) after irradiation of HNM, and (······) *ca.* 24 hours aged after the irradiation in acetonitrile for HNM ceased.

5-Chloro-2-hydroxytriphenylmethanol (ClHM) and (3-hydroxy-2-naphthyl)-diphenylmethanol (HNM) showed the same type of photochromism as HM and HMM. In the case of HNM, however, an irreversible reaction became important. Figure 5 shows absorption spectra of the colored forms of ClHM and HNM.

TABLE 1. EFFECT OF THE CONCENTRATION OF HM ON THE RELATIVE QUANTUM YIELD; $\phi_{rel}=\phi/\phi(1.39\times10^{-4}\text{M})$

$[\text{HM}]\times10^4$(M)	ϕ_{rel}
1.39	1.0
5.56	0.92
9.72	0.87
13.9	0.97
Mean value	0.94

TABLE 2. EFFECT OF LIGHT INTENSITY ON THE RELATIVE QUANTUM YIELD

I/I_0(%)	ϕ_{rel}
100	1.0
54	1.0
48	1.0
36	1.0
25.9	0.93

Photochemical Reaction, Photo and Thermal Bleaching at Room Temperature. Tables 1 and 2 show the effect of the concentration and light intensity on the quantum

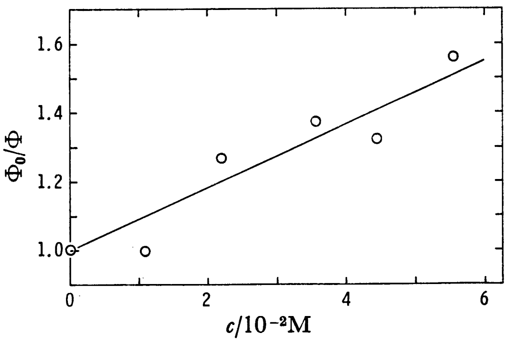


Fig. 6. Quenching by biacetyl in acetonitrile.

yield of the photochemical reaction, HM to F, in acetonitrile. Both concentration and light intensity do not affect the quantum yield, so that the reaction is a one-photon process. The result of the quenching of the photochemical reaction by biacetyl is given in Fig. 6. Quenching by piperylene is very small, if any occurs at all, whereas biacetyl quenches the photochemical reaction significantly. Since piperylene can quench only the triplet state of HM, whereas biacetyl quenches both singlet and triplet states, the state quenched by biacetyl must be the singlet state. The lifetime of the excited singlet state was estimated to be 0.54 ns from the slope of Φ_0/Φ *vs.* concentration of biacetyl in Fig. 6 with the assumption that quenching occurs at the diffusion-controlled rate.

A reactive singlet state with a short lifetime is consistent with the observation that the photochemical reaction occurs even in air-saturated solutions and that no transient intermediate was observed by conventional flash photolysis. Since triphenylmethyl radical is produced from the triplet state,[11,12] HM radical is not a reaction intermediate. Other species, such as phenoxy radical and phenoxy anion derivatives, are not intermediates, since in triphenylmethane derivatives C–H bond cleavage at the central carbon atom generally occurs,[1] and no transient was observed by flash photolysis. Therefore, the photoreaction of HM occurs by a one-step process.

Irradiation by 365 nm light which is absorbed solely by the colored form F accelerates the bleaching of F. This photobleaching occurs not only in air-saturated solutions but also in nitrogen-saturated solutions. The rate constant for thermal bleaching is the same in air and nitrogen-saturated solutions, and also the same before and after the 365 nm irradiation. During the irradiation photo and thermal bleaching occur simultaneously and independently. The rate of bleaching of F is given by

$$-\frac{\mathrm{d}C_F}{\mathrm{d}t} = \phi'' I_0'(1-10^{-OD})\frac{\varepsilon_F C_F}{OD}\times 10^3 + kC_F \qquad (1)$$

where ε_F is the molar extinction coefficient, OD is the optical density, I_0' is the light intensity at 365 nm, ϕ'' is the quantum yield of photobleaching, k is the thermal bleaching rate constant, and C_F is the concentration of F. Integration of Eq. (1) leads to

$$\ln\frac{OD_F^0}{OD_F} - kt = \phi'' I_0' \varepsilon_F \times 10^3 \int (1-10^{-OD})\frac{\mathrm{d}t}{OD} \qquad (2)$$

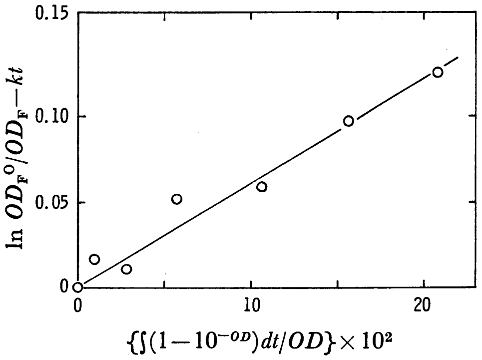


Fig. 7. Plot of $\ln OD_F^0/OD_F - kt$ *vs.* $\{\int(1-10^{-OD})\,\mathrm{d}t/OD\}\times 10^2$ in acetonitrile. Suffix, F, stands for the colored form. The exciting wavelength is 365 nm.

where OD_F^0 is the initial optical density. Evaluation of the integral part of Eq. (2) was performed graphically. Plots of ($\ln OD_F^0/OD_F - kt$) *vs.* $\int(1-10^{-OD})\mathrm{d}t/OD$ are presented in Fig. 7. Using ε_F determined by a method described later, ϕ's were estimated to be 0.0079 for air-saturated and 0.12 for nitrogen-saturated solutions. The large discrepancy in the quantum yields means that the reaction of the triplet state of F is the major process in the photobleaching.

When the photochemical reaction of HM is in equilibrium with the photo and thermal bleaching reactions, Eq. (3) holds.

$$I_0(1-10^{-OD})\frac{\varepsilon C}{OD}\times 10^3 = \phi' I_0(1-10^{-OD})\frac{\varepsilon_F' C_F}{OD}\times 10^3 + kC_F \qquad (3)$$

where ε and ε'_F are the molar extinction coefficients of HM and F at 253.7 nm, C is the concentration of HM, ϕ and ϕ' are the quantum yields of photochemical reaction of HM and photobleaching of F, OD is the optical density at 253.7 nm, and I_0, the light intensity at 253.7 nm. Since the irreversible portion of the photochemical reaction of HM is quite small, $C_0 = C + C_F$ holds approximately, where C_0 stands for the initial concentration of HM. Then Eq. (3) is reduced to:

$$\frac{C_0}{OD_F^\lambda} = \frac{1}{\varepsilon_F^\lambda}\left(1+\frac{\phi'\varepsilon_F}{\phi\varepsilon}\right) + \frac{kOD}{\varepsilon_F^\lambda \varepsilon \phi I_0(1-10^{-OD})\times 10^3} \qquad (4)$$

where the superscript λ represents a value at a wavelength λ. Since, it is probable that ϕ' is not so different from the ϕ'' determined already, $\phi'\varepsilon_F/\phi\varepsilon$ may be very small compared to 1. Thus, Eq. (4) may be simplified to

$$\frac{C_0}{OD_F^\lambda} = \frac{1}{\varepsilon_F^\lambda} + \frac{kOD}{\varepsilon_F^\lambda \varepsilon \phi I_0(1-10^{-OD})\times 10^3} \qquad (5)$$

An analysis at 340 nm is given in Fig. 8. ε_F^{340} was determined to be 4.76×10^3. ϕ was found to be 0.62. The same value of ϕ was obtained at 440 nm. The fairly high value of the photochemical quantum yield in aerated solution provides further evidence that the reactive state is predominantly the excited singlet state.

Photochemical Reaction at 77 K. The absorption spectra of the photoproducts from HM in methanol–

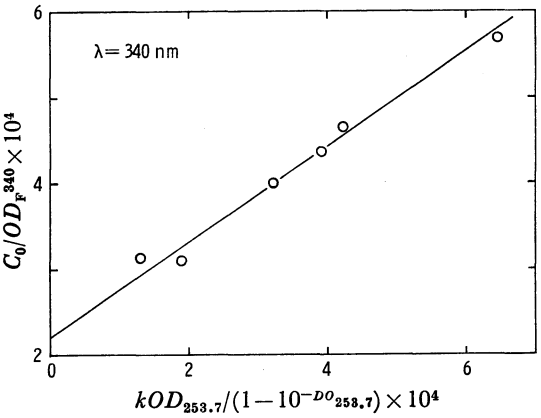


Fig. 8. Plot of $C_0/OD_F^{340} \times 10^4$ vs. $kOD_{235.7}/(1-10^{-OD_{253.7}}) \times 10^4$ in acetonitrile. C_0, k, OD^{340} and $OD_{253.7}$ are the initial concentration of HM, the bleaching rate constant, the optical density of the colored form at 340 nm and the optical density at 253.7 nm.

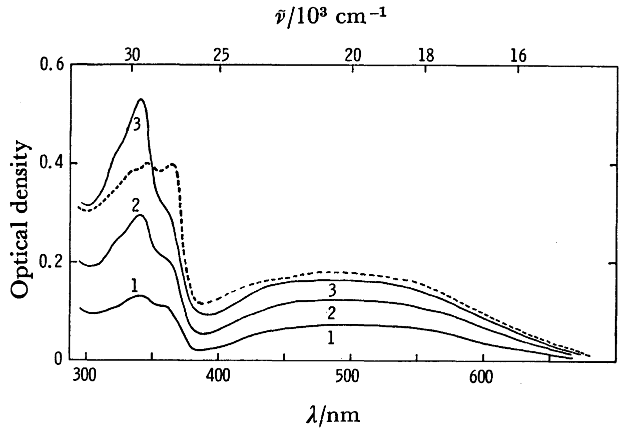


Fig. 9. Absorption spectra of the irradiated HM in methanol–ethanol (1:1) at 77 K; 1— after 10 minute irradiation, 2—35 minutes, 3—115 minutes; ---- cooled to 77 K immediately after melting the solution.

ethanol mixture (1: 1 in volume) at 77 K are shown in Fig. 9 for different irradiation times. The increase in optical density at 340 nm is larger than that at 480 nm indicating that the product is not a single species, since HM has no absorption in this wavelength region. The irradiated glassy solution was allowed to melt and cooled to 77 K again immediately. The resulting absorption spectrum is the dotted curve in Fig. 9. The decrease in optical density around 340 nm is appreciable. 2-Methoxytriphenylmethyl radical obtained by irradiation of 2-methoxytriphenylmethanol under the same conditions as for HM has an absorption maximum at 338 nm. Hence, the absorption around 340 nm belongs to 2-hydroxytriphenylmethyl radical (HM radical) generated photochemically. This conclusion is also supported by the ESR spectra. The irradiated HM solution shows ESR signals which can be assigned to methanol, ethanol, formyl, and HM radicals. All these signals disappear upon melting of the solution, and do not reappear on freezing the solution again.

The solution initially irradiated by 253.7 nm was further irradiated by the light from a superhigh pressure mercury lamp filtered by either a Toshiba VY-43 (transmits longer than —430 nm) or a photographic plate (longer than —300 nm). No change in the absorption spectrum was observed, so that the mechanism by which HM radical is produced by hydrogen atom abstraction of excited F from the surrounding solvent molecules may be almost excluded. It might be possible, however, that F excited by 253.7 nm abstracts hydrogen and that another kind of biphotonic process occurs on 253.7 nm irradiation.

The formation of F is a one-photon process as it is at room temperature, since the yield of F at the early stage of the reaction is proportional to the light intensity.

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