Thermal Bleaching of the Colored Form in the Photochromism of 2-Hydroxy-2′,4,4′-trimethoxytriphenylmethanol in Acetonitrile

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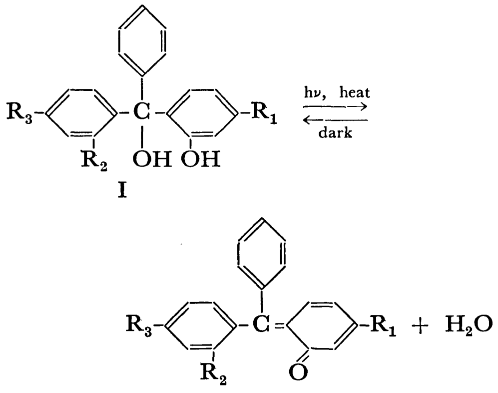
(Received November 1, 1974)

The photochromism of 2-hydroxy-2′,4,4′-trimethoxytriphenylmethanol (HTMM) in acetonitrile differs from that of other 2-hydroxytriphenylmethanol derivatives in some aspects. The colored form, 2′,4,4′-trimethoxy-*o*-fuchsone (TMF), of HTMM partly converts to 2-hydroxy-2′,4,4′-trimethoxytriphenylmethyl cation (Cat) at an early stage of the bleaching reaction. At a later stage a slow bleaching of TMF to HTMM becomes the main decay process. Bleaching of the produced Cat is so slow that Cat remains even after complete disappearance of TMF. The formation of Cat was concluded to be a reaction between adsorbed TMF and water on the cell surface. The rate determining step is not a diffusion process since the activation energy found is much larger than that of viscosity. Cat decays by the reaction with water, not with hydroxide ion.

2-Hydroxytriphenylmethanol derivatives show photochromism[1] as well as thermochromism.[2] The reaction scheme is as follows:



Ia $R_1=R_2=R_3=H$, 2-hydroxytriphenylmethanol (HM)
Ib $R_1=OCH_3$, $R_2=R_3=H$, 2-hydroxy-4-methoxy-triphenylmethanol (HMM)
Ic $R_1=R_2=R_3=OCH_3$, 2-hydroxy-2′,4,4′-trimethoxy-triphenylmethanol (HTMM)
IIa $R_1=R_2=R_3=H$, *o*-fuchson (F)
IIb $R_1=OCH_3$, $R_2=R_3=H$, 4-methoxy-*o*-fuchson (MF)
IIc $R_1=R_2=R_3=OCH_3$, 2′,4,4′-trimethoxyfuchson (TMF)

The colored form of HM, F, decays according to pseudo-first order kinetics.[1] However, MF, the colored form of HMM, shows an unusual bleaching pattern in saturated hydrocarbons such as *n*-hexane, but in polar solvents the bleaching reaction becomes the pseudo-first order.[3] Both substituents and solvent polarity have a critical effect on the bleaching mechanism. TMF which has three electron donating methoxy groups shows no unusual bleaching pattern in *n*-hexane as in the case of MF. However, in acetonitrile it was found to decay in a different pattern. We have investigated the thermal bleaching of TMF in acetonitrile in detail, the reuslts being given in the following.

Experimental

HTMM was synthesized from 2-hydroxy-2′,4,4′-trimethoxybenzophenone by the Grignard reaction with phenylmagnesium bromide and recrystallized several times from ether-*n*-hexane and ethanol-water mixtures. 2-Hydroxy-2′,4,4′-trimethoxybenzophenone was synthesized from 3-methoxyphenol and 2,4-dimethoxybenzoic acid in the presence of boron trifuoride-ethyl ether complex.[4] HTMM; mp 129—131 °C. Found: C, 72.34; H, 6.29%. Calcd for $C_{22}H_{22}O_5$: C, 72.10; H, 6.06%.

Acetonitrile was distilled over phosphorous pentoxide. A 6 W germicidal mercury lamp was used as a light source for 253.7 nm illumination. Absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. A Haake FJ regulater was employed for temperature control.

The initial concentrations of HTMM were chosen to be *ca.* 2×10^{-4} M in all the experiments. The illuminated sample solutions were shaken before the measurements in order to make the concentration of TMF in the cell uniform.

Results and Discussion

The absorption spectral change with time for the solution of HTMM in acetonitrile after illumination for 20 s is shown in Fig. 1. Beside the absorption of TMF there is an absorption band due to other species at 438 nm. This band increases rapidly at the expense of the TMF band with isosbestic points at 420 and 456 nm at an early stage of bleaching. After the absorbance at 438 nm attains maximum, the absorption band due to TMF decreases slowly. The 438 nm band reamins even after TMF has disappeared completely. This absorption spectrum is iden-

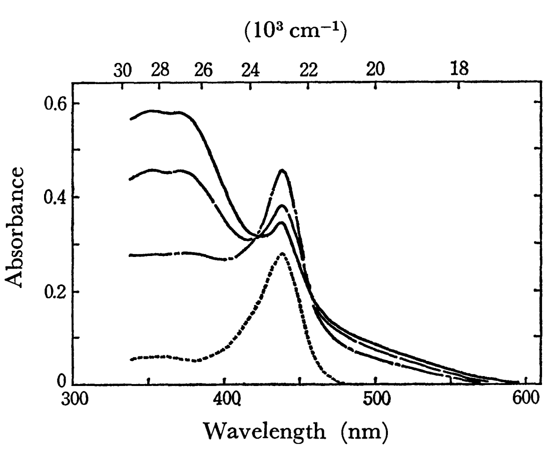


Fig. 1. Spectral change of the colored form of HTMM in acetonitrile.
——; immediately after illumination, — —; 4 min after, —·—; 14 min after, ----; 14 min after.

tical with that of 2-hydroxy-2′,4,4′-trimethoxytriphenylmethyl cation (Cat) prepared by adding sulfuric acid or an oxidizing agent to the HTMM acetonitrile solution. Only TMF is produced photochemically, since the absorption band of Cat does not appear by illumination of HTMM at 77 K.

Since the absorption spectra of TMF and Cat are superposed immediately after illumination, we should know the shapes of individual absorption spectra in order to analyze the growth and the decay of individual species. The absorption spectrum of Cat is known. The absorption spectrum of TMF was obtained by addition of triethylamine to the illuminated solution. Triethylamine forms a colorless complex with Cat selectively. Similar complexing phenomena are reported between crystal violet and primary amines and other triphenylmethyl cation derivatives and amines.[5] The resulting absorption spectrum of THF is given in Fig. 2.

Simultaneous measurement of absorbances at two different wavelengths discriminates the contribution of individual species to the measured absorbances. The wavelengths at 350 nm and 438 nm were chosen which correspond respectively to the absorption maxima of TMF and Cat. The absorbances of TMF and Cat as functions of time are plotted in the logarithmic scale in Fig. 3. The rapid growth of Cat corresponds to the initial decrease of TMF. Mechanical shaking of a sample cell at the stage where Cat is growing causes an increase in the absorbance of Cat and a slight decrease in the absorbance of TMF (Fig. 4). A similar phenomenon was also observed at 35 °C.

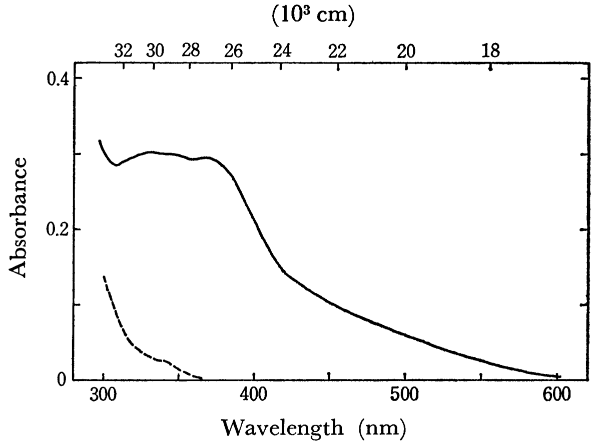


Fig. 2. ——; absorption spectrum of TMF in acetonitrile containing 7.2×10^{-2} M triethylamine, ----; *ca.* 24 hr illumination.

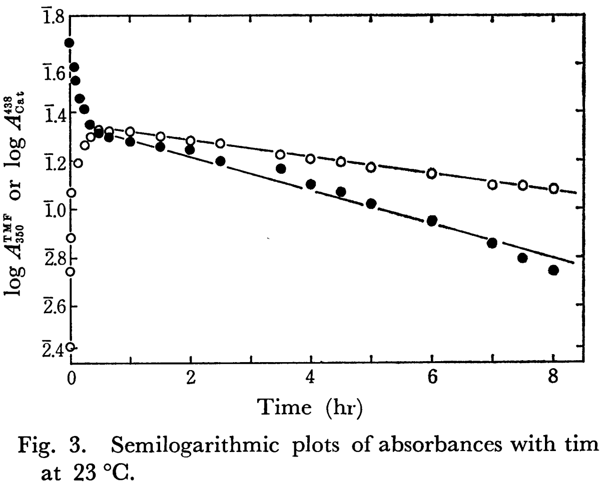


Fig. 3. Semilogarithmic plots of absorbances with time at 23 °C.
●: TMF, ○: Cat.

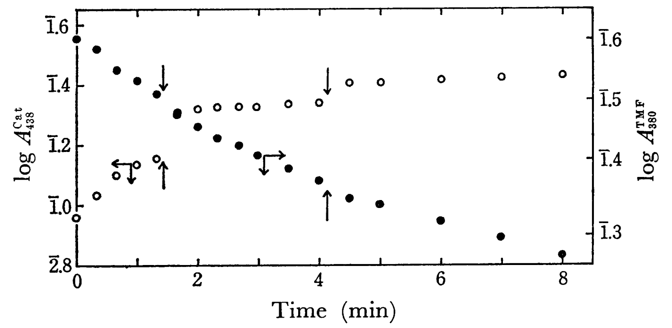


Fig. 4. Absorbance changes of TMF and Cat at the initial period of the reaction at 23 °C.
Arrows indicate the points at which a sample cell was shaken.
●; TMF, ○; Cat.

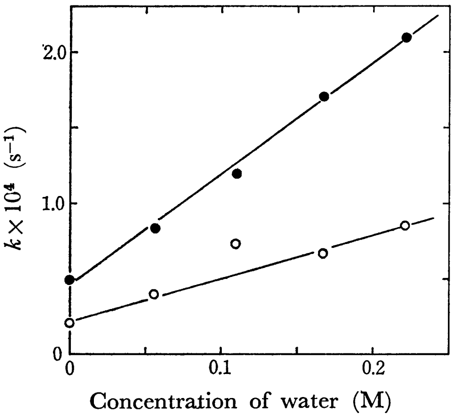


Fig. 5. Effect of water on the decay rates of TMF and Cat.
●: TMF, ○: Cat.

In the later stage both TMF and Cat show the first order decay (Fig. 3). In acetonitrile containing water less than 0.3 M, the type of concentration change of TMF and Cat is similar to that in neat acetonitrile. The first order decay rate constants for TMF and Cat at the later stage are proportional to the concentration of water added (Fig. 5).

With increasing water concentration, the concentration of Cat immediately after illumination becomes so high that the growth of Cat can not be followed. Moreover, the concentrations of TMF and Cat change in a complicated way.

In the solution containing a small amount of water, Cat seems to react with water yielding a starting material HTMM. This differs from other triphenylmethane cation dyes which react with anion to give their leuco forms.[6,7] The formation of Cat occurs only in the initial stage of the TMF decay. This suggests that the reaction is a kind of an inhibited reaction.

The molar absorption coefficient of TMF is not known. It seems to be of the order of 10000 at 350 nm, since that of an analogous compound F is 7830 at the absorption maximum at 77 K in methanol–ethanol (1 : 1). The molar absorption coefficient of Cat was found from the chemically prepared Cat solution to be 62200, being more than six times larger than that of TMF. Since the amounts of the decrease and increase in the absorbances, respectively, of TMF and Cat do not differ significantly from each other at the initial stage, it is probable that a part of TMF converts to Cat and another portion to HTMM.

An effect of mechanical stirring indicates that TMF reacts with water on a cell surface to give Cat. When TMF and Cat occupy the same adsorption sites, the adsorbed amount are given by $[\mathrm{Cat}]_{\mathrm{ads}}=\alpha_1[\mathrm{Cat}]/(1+\beta_1[\mathrm{Cat}]+\beta_2[\mathrm{TMF}])$ for Cat and $[\mathrm{TMF}]_{\mathrm{ads}}=\alpha_2[\mathrm{TMF}]/(1+\beta_1[\mathrm{Cat}]+\beta_2[\mathrm{TMF}])$ for TMF, respectively, where α's and β's are constants. If Cat is adsorbed much more strongly than TMF, the adsorbed amount of TMF can be given by $[\mathrm{TMF}]_{\mathrm{ads}}=C[\mathrm{TMF}]/[\mathrm{Cat}]$, where C is a constant. Hence, the reaction rate is given for TMF by Eq. 1 and for Cat by Eq. 2.

$$-\frac{\mathrm{d}[\mathrm{TMF}]}{\mathrm{d}t} = k_1\frac{[\mathrm{TMF}][\mathrm{H_2O}]}{\mathrm{Cat}} + k_1'[\mathrm{TMF}][\mathrm{H_2O}] \qquad (1)$$

$$\frac{\mathrm{d}[\mathrm{Cat}]}{\mathrm{d}t} = k_2\frac{[\mathrm{TMF}][\mathrm{H_2O}]}{[\mathrm{Cat}]} - k_2'[\mathrm{Cat}][\mathrm{H_2O}] \qquad (2)$$

At the initial stage of reaction, the second terms of the right hand of Eqs. 1 and 2 can be neglected as compared with the first terms. The concentration of water is expected to be practically unchanged. Thus we obtain

$$\ln([\mathrm{TMF}]/[\mathrm{TMF}]_0) = -k_{\mathrm{TMF}}\int \mathrm{d}t/[\mathrm{Cat}] \qquad (3)$$

$$[\mathrm{Cat}]^2 - [\mathrm{Cat}]_0^2 = k_{\mathrm{Cat}}\int [\mathrm{TMF}]\mathrm{d}t \qquad (4)$$

Plots according to Eqs. 3 and 4 are linear (Figs. 6 and 7, respectively), indicating that the proposed mechanism is highly probable. The activation energies for k_{TMF} and k_{Cat} were found to be 17.8 and 25.6 kcal/mol, respectively, considerably larger than that of viscosity for acetonitrile, 0.8 kcal/mol. The rate determining step is, therefore, not diffusion process unlike the bleaching reaction of MF in *n*-hexane. A mechanical stirring may cause a forced convection which accelerates the reaction between TMF and water on a cell surface. Thus, the absorbance of TMF decreases in smaller amount than the corresponding increase in the absorbance of Cat, being consistent with the larger molar absorption coefficient of Cat.

Equations similar in form to Eqs. 3 and 4 can be derived from another mechanism in which dissociated proton from water reacts with TMF to give Cat in acetonitrile instead of on the cell surface. However, this is not the case, since the presence of sulfuric acid affects neither the growth rate now the initial yield of Cat when the acid concentration is lower than 2×10^{-5} M. A feature differing from the neat acetonitrile solution is that the growth of Cat is not monotonic but stepwise. The reason for the stepwise growth is not clear at all. In the solution containing acid of higher concentration, a considerable amount of Cat is produced immediately by the addition of acid.

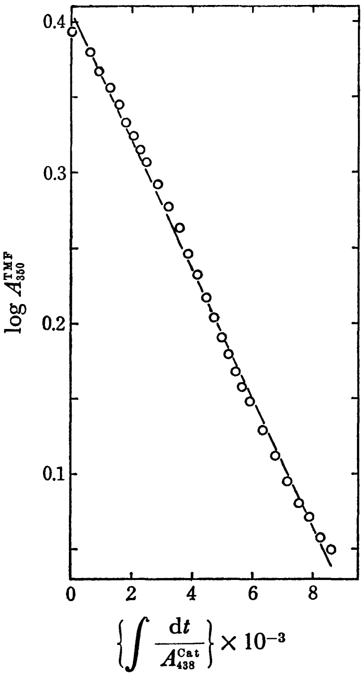


Fig. 6. Reaction analysis of TMF at the initial period at 23 °C.

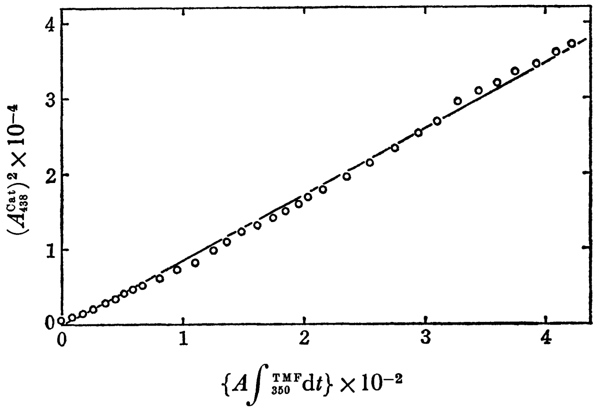


Fig. 7. Reaction analysis of Cat at the formation period at 23 °C.

The decay rate of TMF at the later stage is faster in solutions containing aqueous sulfuric acid as compared with solutions containing the same amount of water. The effect of added acid is not the simple protonation of TMF to give Cat, since Cat also decays. The following may be a possible reaction:

$$\mathrm{TMF} + (\mathrm{H_3O^+})_{\mathrm{solv}} \rightarrow \mathrm{HTMM} + (\mathrm{H^+})_{\mathrm{solv}}.$$

The decay rate of Cat, however, is slower in acidic solutions. The slower decay of Cat may be due to the slow production of Cat from the reaction between acid and HTMM. An enhanced stability of Cat in acidic solution may also be responsible.

In solutions containing triethylamine, the absorption due to Cat does not appear, although the bleaching pattern of TMF is the same as in neat acetonitrile. Cat once produced, therefore, is complexed with triethylamine quickly. The resulting complex cation would be adsorbed on the cell surface as in the case of Cat. Consequently, the bleaching pattern of TMF is the same as in solution without triethylamine. The decay rate of TMF at the later stage is proportional to the triethylamine concentration. The reaction $TMF + (Et)_3N \cdot H_2O \rightarrow HTMM + (Et)_3N$ is plausible.

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