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Thermal Decay of the Colored Form in Photochromism of 2-Hydroxy-4-methoxytriphenylmethanol in *n*-Hexane

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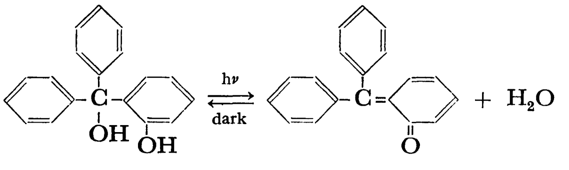
It was found that, like 2-hydroxytriphenylmethanol (HM), 2-hydroxy-4-methoxytriphenylmethanol (HMM) shows photochromism as well as thermochromism. Photo- and thermochromism of HMM occur even in *n*-hexane, in which a photochemical irreversible reaction occurs for HM. In *n*-hexane solution of HMM, a three-stage thermal fading pattern was observed at room temperature and at lower temperatures, the pattern becoming a one-stage type at a higher temperature. Mechanical stirring of a sample solution caused a decrease in the concentration of the colored form in *n*-hexane at room and lower temperatures but not at a higher temperature. These phenomena are caused by the backward reaction on the wall of a sample cell including diffusion as the rate-determining step. In *n*-hexane–dimethoxyethane (or acetonitrile) mixed solvents, the first-order rate constant becomes smaller with increase in the dimethoxyethane (or acetonitrile) concentration. From a certain concentration, shaking of a cell causes no decrease in the concentration of the colored form.

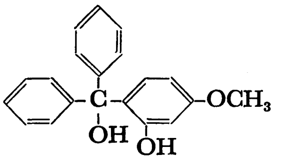
2-Hydroxytriphenylmethanol (HM) is known to show thermochromism.[1] It also shows photochromism, its reaction being shown by the following scheme.[2]



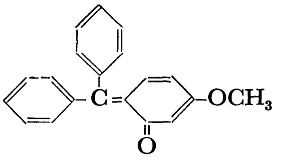
(HM)

Scheme 1.

At room temperature, HM shows photochromism in acetonitrile, ethyl ether, dimethoxyethane, benzene and 1,2-dichloroethane but only an irreversible reaction occurs in saturated hydrocarbon. Like HM, 2-hydroxy-4-methoxytriphenylmethanol (HMM) shows photochromism and thermochromism in these solvents. Photochromism occurs even in *n*-hexane, cyclohexane and methylcyclohexane, thermochromism being also observed in these solvents.



(HMM)



(MF)

The behavior of the thermal decay of the colored form, *p*-methoxy-*o*-fuchsone (MF) in these hydrocarbon solvents is very curious differing from that in other solvents such as acetonitrile, ethyl ether. In order to make clear this curious behavior the thermal decay was followed under different conditions.

Experimental

Materials. 2-Hydroxy-4-methoxytriphenylmethanol was synthesized by the Grignard reaction of 2-hydroxy-4-methoxybenzophenone and phenylmagnesium bromide and purified by repeated recrystallization from an ether–*n*-hexane mixture and a methanol–water mixture after being treated with activated charcoal. *n*-Hexane, cyclohexane and methylcyclohexane were treated with fuming sulfuric acid diluted with concentrated sulfuric acid for a long time, washed with water, neutralized with an aqueous alkaline solution, treated with alkaline potassium permanganate, washed again with water, and then dried over calcium chloride. They were finally distilled over sodium wire. Acetonitrile was distilled over phosphorus pentoxide. Dimethoxyethane was dehydrated for several months over sodium-potassium alloy after evacuation.

The concentration of HMM was *ca.* 2×10^{-4} M in all the experiments.

Apparatus. A 6 W germicidal mercury lamp was used as a light source. The absorption spectrum was measured with a Hitachi EPS-3T spectrophotometer. The thermal decay was followed at 340 nm on the same instrument. Haake-FJ was used for temperature control.

Results

General Aspect of the Thermal Decay. MF appeared when the *n*-hexane solution of HMM was irradiated at 253.7 nm. The absorption spectrum of MF in *n*-hexane is shown in Fig. 1. The absorption maxima in *n*-hexane shift to shorter wavelength than those in acetonitrile or ethyl ether. In acetonitrile or ethyl ether an irreversible photo-product was formed in a small amount, but in saturated hydrocarbon the absorption spectrum after the termination of the thermal decay agreed almost completely with that of unirradiated HMM. The concentration of MF produced

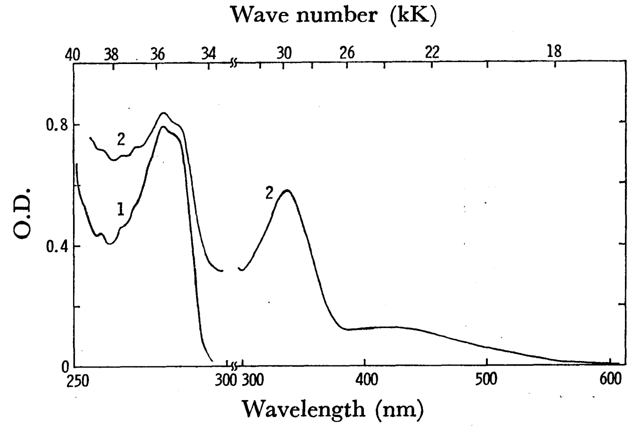
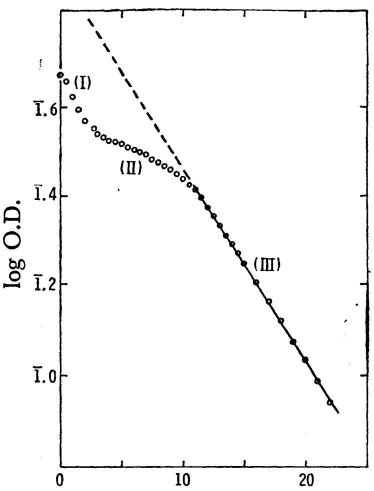


Fig. 1. Absorption spectrum of HMM in *n*-hexane.
1: Before irradiation, 2: After irradiation

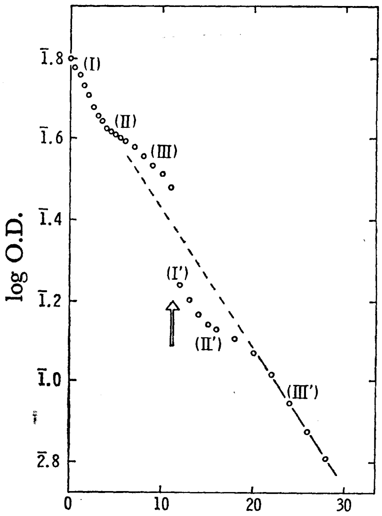


Time (min)

Fig. 2. Three-stage thermal decay of the colored form, MF, in *n*-hexane at 22 °C.

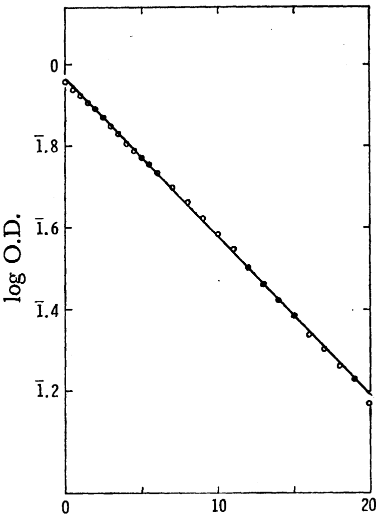
is the order of 10^{-5} M, water being also produced in the same concentration as in the case of HM (Scheme 1).

Mechanical stirring of a sample solution markedly decreases MF concentration. The thermal decay of MF was followed after the sample cell had been shaken. The decay rate decreased gradually after several minutes and became greater again approaching a constant value. The same phenomenon occurred each time the cell was shaken. The three-stage thermal decay after shaking is shown in Fig. 2. The decay pattern was identical within the optical density range of MF *ca.* 1.5—*ca.* 0.3 at 340 nm. The rate of decay of stage I is almost the same as that of III, the rate of stage II being smaller than that of I and III. A satisfactory first-order decay is seen at stage III. When a cell was shaken at stage III, a change was observed in which the rate constants at stages III and III′ agreed with each other fairly well (Fig. 3). The absorption spectrum is identical at any stage of the thermal decay. Consequently, no stable intermediate other than MF is involved in the thermal fading reaction in *n*-hexane. Oxygen would not be involved in it since the decay pattern was the same as that of the air saturated solution when the decay was followed after deoxygenation of the solution by bubbling nitrogen.



Time (min)

Fig. 3. Thermal decay of the colored form, MF, in *n*-hexane at 12 °C.
An arrow shows the point at which a sample cell was shaken.



Time (min)

Fig. 4. One-stage thermal decay of the colored form, MF, in *n*-hexane at 36 °C.

Temperature Effect. The three-stage thermal fading pattern was observed at room temperature and lower temperatures, but at a higher temperature, *e.g.* at 36 °C, the pattern changed and an ordinary first-order decay was observed from the beginning (Fig. 4). Mechanical stirring of a cell in the course of decay does not accelerate the decrease of the concentration of MF. From the temperature dependence of the rate constant at III, the activation energy for the reaction was evaluated to be 1.7 kcal/mol, which agrees with the activation energy for the viscosity of *n*-hexane. Although the first-order decay was observed from the beginning at 28 °C, the decay pattern is a mixed type of the three-stage pattern and the ordinary first-order decay pattern (one-stage decay pattern), since shaking of a cell in the course of the decay slightly decreases the optical density of MF.

Addition Effect of Dimethoxyethane and Acetonitrile. The decay pattern of MF changes gradually from a three-stage to a one-stage type in the mixed solvent *n*-hexane–dimethoxyethane (or acetonitrile) with the increase of the dimethoxyethane (or acetonitrile) concentration. The decay rate constant also decreases at the same time. The relationship between the rate constant and the concentrations of dimethoxyethane and acetonitrile is shown in Fig. 5.

Thermal Decay in Water Saturated n-*Hexane Solution.* In acetonitrile or ethyl ether, the thermal decay rate constant of the colored form of HM or HMM is proportional to the concentration of the water added. However, in *n*-hexane saturated with water the decay pattern is the same as that in ordinary *n*-hexane, *i.e.*,

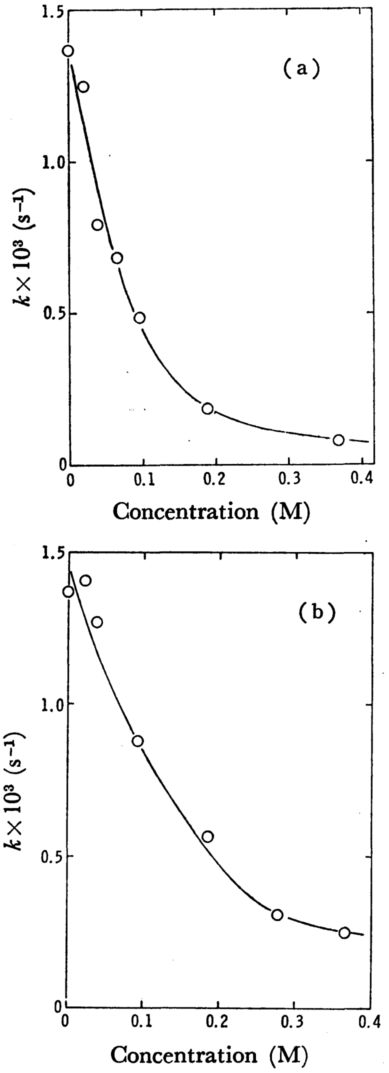


Fig. 5. (a) Dependence of the decay rate constant on the concentration of dimethoxyethane at 22 °C.
(b) Dependence of the decay rate constant on the concentration of acetonitrile at 22 °C.

the three-stage decay pattern changes to one-stage decay type with the rise of temperature. The rate constant 1.48×10^{-3} s^{-1} was nearly the same as that in ordinary *n*-hexane, 1.37×10^{-3} s^{-1}.

In the case of *n*-hexane solution saturated with water in a cell whose surface was damped with water, the decay pattern was the one-stage type and a shaking did not decrease the concentration of MF. This rate constant was about 1/20 as compared with a no-damped experiment.

Discussion

In *n*-hexane, the reaction mechanism of the thermal decay is quite different from that in acetonitrile and ethyl ether. The reaction system is never homogeneous. Dissolved water in cyclohexane or benzene does not exist as the associated forms such as dimer or trimer, but as a monomer.[3] It is highly probable that dissolved water in *n*-hexane exists as a monomer. Since the same decay pattern was observed in cyclohexane as well as *n*-hexane, the associated form of water would not be involved in the thermal fading reaction.

Adsorbed water on the surface of a quartz cell is considered to react with MF, but it is not clear whether MF is adsorbed or not. This is the diffusion-controlled reaction since the rate hardly changes with the concentration of dissolved water in *n*-hexane and a shaking of a cell accelerates the fading of MF. The concentration gradient on the surface of the cell is given by

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{{}^{*}c - {}^{0}c}{\sqrt{\pi D t}}$$

where $\sqrt{\pi D t}$ represents the thickness of the diffusion layer. The thickness of the diffusion layer depends on time in the system in which only diffusion occurs. Usually natural convection occurs because of the density gradient by the reaction on the surface, and then the thickness of the diffusion layer is constant after a certain period.[4] If we denote the thickness of the diffusion layer by δ, the concentration gradient is given by

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{{}^{*}c - {}^{0}c}{\delta}$$

Since the reaction on the surface is fast in comparison with diffusion, ${}^{0}c = 0$. Thus the concentration gradient on the surface of the cell is expressed simply as follows.

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{{}^{*}c}{\delta}$$

Consequently, the rate formula for the thermal decay is

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = D\frac{A}{V}\frac{c}{\delta} = kc$$

where A is the surface area in contact with solution and V is the volume of solution. A/V is equal to 4.25 cm^{-1} when 4 ml of solution is placed in a cell of 1 cm × 1 cm. For diffusion coefficient D, 10^{-5}—10^{-6} cm^2/s is taken, δ being *ca.* 10^{-3} cm, and for rate constant k, 10^{-2}—10^{-3} s^{-1} is taken. The reaction should be of first order. This satisfactorily elucidates the third stage of the three-stage decay. The diffusion coefficient for a molecule larger than a solvent molecule is given by Einstein's equation

$$D = \frac{kT}{6\pi r \eta}$$

where r is the radius of the diffusing molecule and η is the viscosity of the solvent. The activation energy for the thermal decay rate constant is, then, expected to agree with the activation energy for the viscosity of *n*-hexane. The former is 1.7 kcal/mol and the latter 1.76 kcal/mol, an excellent agreement being seen. Almost the same rate constants in water-saturated *n*-hexane and ordinary *n*-hexane are also understood in view of the diffusion-controlled reaction.

The forced convection by shaking of a cell remains at stage I of the three-stage decay. The convection decreases the thickness of the diffusion layer of MF. The decay is fast at this stage. At stage II, the forced convection gradually subsides and the thickness of the diffusion layer increases, the decay rate becoming small and finally the reaction is governed only by the diffusion of MF. The change from stage II to stage III would be caused by the development of natural convection, which occurs by the accumulation of HMM in the vicinity of the cell surface with the progress of reaction. Natural convection reaches a steady state after a certain period, the thickness of the diffusion layer thus becoming constant and the first-order decay being observed. When compared with stage II the thickness of the diffusion layer decreases at stage III and the decay rate becomes great.

The decrease in diffusion coefficient due to the solvation by dimethoxyethane (or acetonitrile) molecules might make the rate decrease when dimethoxyethane (or acetonitrile) is added. The thermal decay rate decreases rapidly with the increase of the concentration of polar component and approaches a constant value. The switching of the reaction mechanism occurs at about 0.2 M for dimethoxyethane and about 0.3 M for acetonitrile. Above these concentrations, the thermal decay is governed by the one-stage type not controlled by diffusion. The reaction on the surface of a cell is inhibited and the reaction in solution may become the rate-determining step. The result of damped experiment shows that the reactivity of physically adsorbed water is of the same order as that of water in solution.

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