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Convenient Chemical Actinometer with 2-Hydroxy-4′-methoxychalcone[1)]

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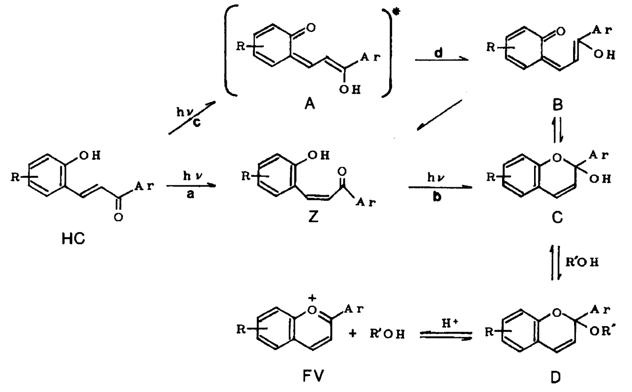
Synopsis. The quantum yields for the photochemical conversion of 2-hydroxy-4′-methoxychalcone into the flavylium ion are in the range of 0.25—0.35 in acetic acid and 0.14—0.2 in aqueous ethanol at pH 2, depending on the wavelength of UV light. The quantum yields are essentially constant against any changes in the light intensity, temperature, or substrate concentration, which is a favorable feature regarding use as a convenient chemical actinometer. A one-photon mechanism involving excited-state proton-transferred tautomer is proposed.

Anthocyanidins (aglycons of anthocyanins) are stable only in strongly acidic media, while naturally occurring anthocyanin pigments are stabilized in essentially neutral media due to copigmentation and/or stacking.[2)] The photochemical conversions of 2-hydroxychalcones were studied earlier by Jurd,[3)] as well as Dewar and Sutherland,[4)] while the thermal conversions were studied by Bruoillard and Dubois,[5)] as well as McClelland et al.[6)] However, systematic or quantitative studies as a photochromic system have been scarecely reported.[7)] This paper is concerned with the application of the photochemical conversion of 2-hydroxy-4′-methoxychalcone (**1**; HC in Scheme 1 with R=H and Ar=*p*-methoxyphenyl) to the 4′-methoxyflavylium ion (**2**; FV with R=H and Ar=*p*-methoxyphenyl) to a chemical actinometer.

Results and Discussion

Quantum Yields for the Photoreaction. Figure 1 illustrates the linear response for the photochemical conversion of **1** to **2** in acetic acid (a), together with the tris(oxalato)ferrate(III) actinometer[8)] (b) and Heller's fulgide actinometer[9)] (c) under complete absorption (99% or more) of the incident 365—366 nm light. Similarly, the linear response of the rate on the irradiation time was obtained with other monochromatic light beams of 334, 313, and 254 nm, respectively. The quantum yields are listed in Table 1 for both an aqueous ethanol solution and an acetic acid solution. In the latter, the colored form **2** was substantially stable both upon heating at 50 °C and upon prolonged irradiation with visible light. In an aqueous ethanol solution at pH 2, however, **2** was thermally bleached, though photochemically inert. Thus, chalcone **1** (curve a) was photochemically converted to **2** (b), which was substantially bleached upon heating at 50 °C (c), as shown in Fig. 2.



Scheme 1. Mechanisms for the photochemical conversion of 2-hydroxychalcones (HC) to flavylium ions (FV).

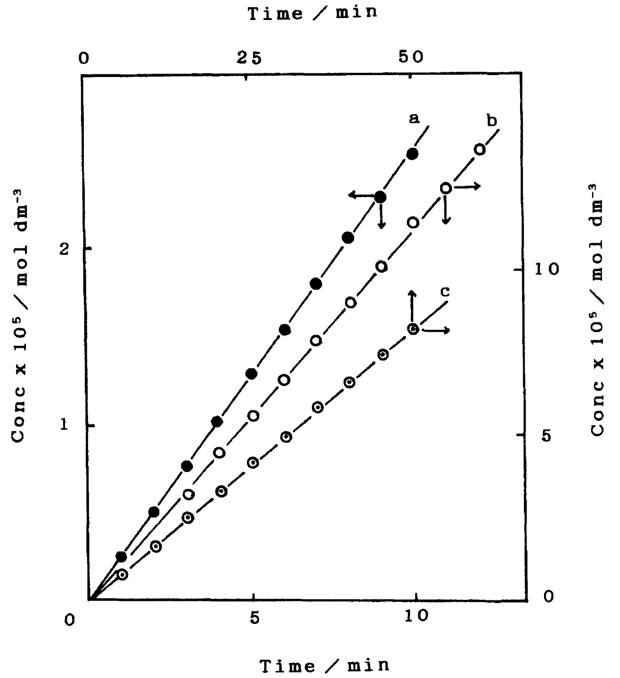


Fig. 1. Linear responses of the photoreactions to the irradiation time under the conditions that the incident light at 365 nm was entirely (<99%) absorbed throughout the reactions. (a) Chalcone **1** in 1.5×10^{-4} in acetic acid, (b) tris(oxalato)ferrate(III) actinometer in 6.0×10^{-3}, (c) Heller's fulgide actinometer in 7.7×10^{-4} mol dm^{-3} in toluene.

Upon subsequent irradiation with UV light, the bleached solution (c) underwent photochemical coloration repeatedly with a quantum yield of 0.16, which was essentially similar to that of the initial solution (0.15). The photoreaction rates were measured as a function of the absorbed light intensity (I_a). Figure 3 shows the linear response of the rate on I_a, indicating

Table 1. Quantum Yields for the Photochemical Conversion of **1** to **2**[a)]

Irrad. light	Medium conditions	
nm	Acetic acid	pH 2 in aq ethanol[b)]
365	0.28	0.15 (0.16)[c)]
334	0.33	0.17
313	0.35	0.21
254	0.31	[d)]

a) Tris(oxalato)ferrate(III) solution was used for actinometry (method A). The concentrations of **2** formed were determined from the absorption at 440 nm and the absorption coefficients 4.27×10^4 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ for acetic acid solution and 3.83×10^4 $\mathrm{mol^{-1}\,dm^3\,cm^{-1}}$ for aqueous ethanol solution at pH 2. b) Aqueous ethanol mixture (1 : 1 in volume). c) Measured after one cycle of photocoloration and thermal decoloration at 50 °C. d) Plots of the concentration of **2** vs. irradiation time was not linear.

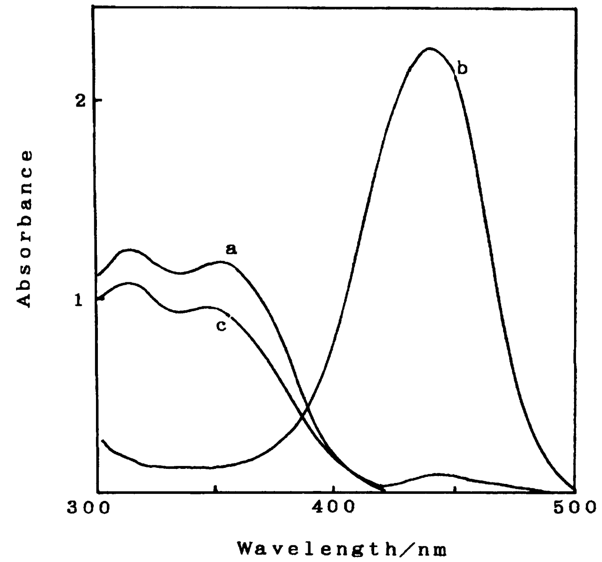


Fig. 2. Absorption spectra of **1** (a) before UV irradiation, (b) at the photostationary state on UV irradiation, and (c) subsequently heated at 50 °C, in 6×10^{-5} $\mathrm{mol\,dm^{-3}}$ in 1 : 1 aqueous ethanol solution at pH 2.

that the quantum yield is independent of I_a.

Suitable Features as Chemical Actinometer. As described above, the quantum yield for the photoreaction of **1** was essentially constant against the light intensity and the irradiation time, which are prerequisite features for use as a chemical actinometer. Furthermore, the absorption spectrum of the photoproduct (**2**) is well separated from that of the reactant (Fig. 2), allowing easy measurement by direct absorption spectroscopy. The quantum yields were essentially constant against the temperature over the 5 to 35 °C range and the concentration of **1** over the range of 10^{-5} to 10^{-2} $\mathrm{mol\,dm^{-3}}$, both in an aqueous ethanol solution at pH 2 and in acetic acid. However, a concentration of **1** not higher than 10^{-3} $\mathrm{mol\,dm^{-3}}$ is recommended, since the

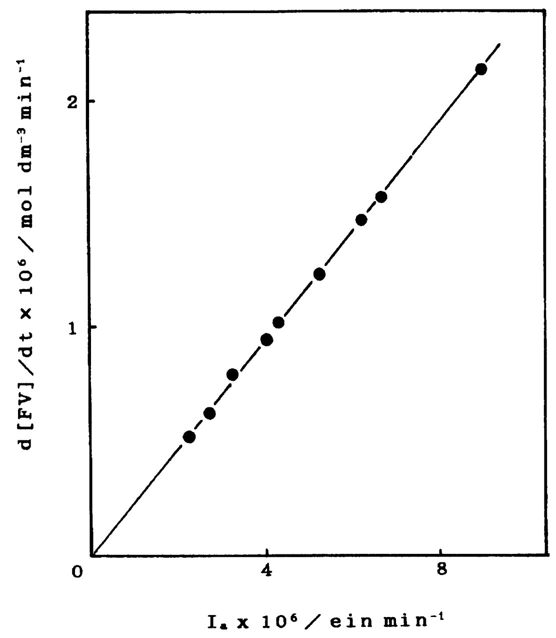


Fig. 3. Plot of the rate for photochemical conversion of **1** to **2** as a function of the absorbed light intensity at 334—366 nm. An acetic acid solution of **1** in 1.5×10^{-4} $\mathrm{mol\,dm^{-3}}$ and a toluene solution of the fulgide actinometer in 1.5×10^{-4} $\mathrm{mol\,dm^{-3}}$ were used in method B.

thermal conversion to **2** was not negligible at a higher concentration, e.g., 10^{-2} $\mathrm{mol\,dm^{-3}}$ in acetic acid at 32 °C upon standing for 10 h in the dark. The photochemical and thermal reactions were not affected by the dissolved oxygen, moisture, or acid impurities. In addition, **1** and **2** are easy to prepare by one-step reactions using inexpensive commertial reagents.

Discussion on the Mechanism. The photoreaction mechanisms may be discussed in terms of one-photon vs two-photon processes (Scheme 1). While the one-photon process includes proton-transferred tautomer A in the excited states (path c), the two-photon process includes *E*/*Z* photoisomerization (path a)[3)] followed by a photocyclization of the rotamer Z (path b).[4)] Though in our previous work[7b)] a two-photon mechanism was tentatively assumed, the possibility of a one-photon mechanism was not ruled out, since it had been established that the acidity/basicity of the intramolecular proton donor/acceptor groups is markedly increased upon photochemical excitation.[10)] In the present work, however, we must reconsider the mechanism. Thus, the kinetic data (Fig. 3) supports the one-photon mechanism, in which tautomer A may undergo a conformational rotation into rotamer B (path d) followed by a 6π-electrocyclic closure to give a hemiacetal C, without any further excitation. Frontier orbitals calculated with the MNDO-PM3 algorithm[11)] also supported the formation of the excited-state proton transfered tautomer A, which will be discussed elsewhere in some detail. The flavylium ion **2** may be formed either by acid-catalyzed dehydration of the hemiacetal C or by the intermediacy of acetal D.

On the other hand, the thermal bleaching (hydration) of **2** can be depicted as a nucleophilic addition of ROH (with HOMO) directly at the C2 position, or indirectly at the C4 position of the pyrylium ring, followed by rapid migration to the C2 position. According to a kinetic study by McClelland and Gedge,[6a)] although initial hydration at the C4 position is kinetically favored, the hydrated product is thermodynamically unstable, so that it is rapidly equilibrated to a mixture of acetal C and chalcone Z in an aqueous solution. The lack of the photochemical bleaching (hydration) of **2** may be explained using a simplified model, as follows. In the lowest excited state, both the LUMO and HOMO are singly occupied, which may be referred to as SOMO and SOMO′, respectively. Of the two, the lower SOMO′ is closer to, and hence, more effectively interacts with the HOMO of nucleophiles (ROH), because of the smaller energy gap.[12)] However, according to the MNDO-PM3 calculation[11)] of **2** with full structure optimization, the coefficients of the SOMO′ were nil or very small at both the C2 and C4 positions; thus, the photochemical hydration would hardly occur.

Experimental

The UV and visible absorption spectra were recorded on a Hitachi 200-10 spectrophotometer, while the ^{1}H NMR spectra were recorded on a Hitachi R-24 spectrometer. The pH values of the solutions were measured both before and after irradiation using a Toadenpa HM 30-S pH meter.

The quantum yields were measured by one of the following methods. In method A, UV irradiation was carried out by means of a Hitachi 204 fluorescence spectrometer, which provided monochromatic light beams from a 120-W high-pressure mercury lamp. The photoreaction vessel was a standard 10 mm-depth square quartz cell, and was placed in the sample chamber of the apparatus. In method B, up to 10 samples were irradiated in identical Pyrex tubes (ca. 5 cm^3) in parallel with a merry-go-round irradiation apparatus in a thermostat. The UV light source was a 100-W high-pressure mercury lamp (Rico Kagaku), and light beams of 313—366, 365—366, 405—436, or 545 nm were respectively isolated by utilizing suitable combinations of filters, i.e., Toshiba UVD36C, UV35+UVD36c, UV-39, or a $NiSO_4$ solution. The absorbed light quanta were estimated using a solution of tris(oxalato)ferrate(III) as an actinometer[8)] in method A, while in method B they were estimated using (*E*)-2-[1-(2,5-dimethyl-3-furyl)ethylidene]-3-isopropylidenesuccinic anhydride (ϕ 0.185 in toluene unstirred during photolysis) as an actinometer.[9)] In an experiment concerning the effects of the incident light intensity, the intensities were graded by lapping the reaction tubes with a semi-transparent polyethylene film several folds. The solution of **1** was irradiated without elimination of the dissolved oxygen.

The solvents were distilled before use. 2-Hydroxy-4′-methoxychalcone (**1**) was prepared by a base-catalyzed aldol condensation in 55% yield,[13)] while 4′-methoxyflavylium perchlorate (**2**) was prepared by an acid-catalyzed condensation,[14)] both from *p*-methoxyacetophenone and salicylaldehyde. Yellow needles of **1**: mp 149—52 °C; ^{1}H NMR (60 MHz, DMSO-d_6) 3.5 (3H, s, OMe), 6.4—8.0 (10H, m, vinyl+aryl), 10.0 (1H, s, OH).

Orange needles of **2**: mp 198—200 (lit, 196—197 °C).[14)] Compound **2** was unstable and turned dark in DMSO-d_6, and was not so soluble in $CDCl_3$.

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