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Bull. Chem. Soc. Jpn., *73*, *2215—2219 (2000)*

Photoreactions of 3-(2-Hydroxyphenyl)-1-(substituted phenyl)-2-propen-1-ones (Substituted 2-Hydroxychalcones) in Organic Solvents in the Presence and Absence of Acid

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(Received March 17, 2000)

Absorption spectra and photochemical reactivities of a dozen 3-(2-hydroxyphenyl)-1-(substituted phenyl)-2-propen-1-ones (substituted 2-hydroxychalcones) have been investigated in organic solvents in the presence and absence of added acid. Upon UV irradiation in the presence of 5 mM perchloric acid, flavylium ions were formed in high quantum yields around 0.34, regardless of the nature of the substituents. Upon irradiation in neutral solution, on the other hand, amino-substituted chalcones gave photo-*Z*-isomers as thermostable products, while the majority of other chalcones gave cyclic hemiacetals (2-hydroxy-2-phenyl-2*H*-1-benzopyranes). The quantum yields for the photochemical *E*/*Z* isomerization in the neutral solution were comparable to those in the acid solution, except for the amino-substituted chalcones which revealed lower quantum yields. Remarkable hypsochromic shifts were observed for the absorption spectra of the amino-substituted chalcones upon addition of acid, reflecting protonation on the amino group.

A new and environmentally suitable photochromic system involving chalcone–flavylium interconversion, as a simplified model of the naturally occurring anthocyanin dyes,[1—3] has some unique features e.g., it works in aqueous and organic solvents[4—6] as well as gel matrices,[7] and photochromic response and color stability are strongly dependent on the acidity of the medium and hence capable of controlling the photochromic properties. Recently, a novel photochemical process has been developed in the system, leading to a photon-mode erasable optical memory with nondestructive readout ability.[8,9]

While the 4′-amino derivatives exhibit excellent color properties (high color purity and strong intensity) and good photochromic reversibility in almost neutral pH region,[10,11] their quantum yields for photochemical coloration are quite low in aqueous ethanol solution. Upon examination of the medium conditions, however, the coloration quantum yields have been markedly improved in aprotic solvents such as tetrahydrofuran or 1,2-dimethoxyethane in the presence of a small amount of acid.[12] The present paper reports on the medium effects on the photochemical reactivities of a series of substituted 2-hydroxychalcones.

Experimental

Electronic absorption spectra were recorded on a Hitachi U-3000 spectrophotometer, while ^{1}H NMR spectra were obtained on a JNM-MY spectrometer (60 MHz). Melting points were measured with a micro-melting point apparatus (Yanaco MP-S3, Yanagimoto). The quantum yields were measured with monochromatic light beams from a 120-W mercury lamp through a diffraction grating of a Hitachi 204 fluorescence spectrophotometer. The photoreaction vessel was a standard 10 mm-depth square cell, which was placed in the sample chamber of the apparatus. The absorbed light quanta were estimated using the potassium tris(oxalato)ferrate(III) actinometer solution,[13] by the method of "total absorption" of incident light.[14] From the slopes of the plots for the flavylium-ion or chalcone absorbances as a function of the irradiation time, amounts of the flavylium ions or chalcones were determined by using the estimated molar absorption coefficients (values are shown in Table 2 in the next section). In order to minimize the errors which might be caused by the secondary photoreactions and/or light absorption of the primary photoproducts, photochemical conversions were usually controlled below 5%. Reactions were carried out without elimination of the dissolved oxygen, while fresh solvents of guaranteed grade (Wako Chemicals) were used as received. 3-(2-Hydroxyphenyl)-1-(substituted phenyl)-2-propen-1-ones (substituted 2-hydroxychalcones) were prepared by a base-catalyzed aldol condensation[15] while flavylium perchlorates were prepared by an acid catalyzed condensation,[16] both starting from substituted acetophenones and salicylaldehyde. Melting points and ^{1}H NMR data are listed in Table 1 together with the yields of pure crystals.

Results and Discussion

Figure 1 compares photochemical reactions of the parent 2-hydroxychalcone (**1**) in 1,2-dimethoxyethane (DME) solution in the presence and absence of added acid, on irradiation with 365—366 nm light. Thus, in the presence of 5 mM perchloric acid (a), the absorption bands of chalcone **1** decrease and a new band of the flavylium ion appears around 400 nm with an isosbestic point around 360 nm (and 270 nm). On prolonged irradiation a photostationary state (PSS) is attained, and from its maximum absorbance (A_{PSS}) an approximate molar absorption coefficient ($\varepsilon_{\max}$) is esti-

Table 1. Yields and Physical Properties of the 2-Hydroxychalcones

2-Hydroxychalcone	Yield[a)]	Appearance and melting point	^{1}H NMR (DMSO-d_6, 60 MHz)
R	%	°C	δ/ppm
4′-NEt$_2$	17.0	Yellow plates (ethanol); 172.0—174.1	1.14 (t, 6H, J = 6 Hz), 3.50 (q, 4H, J = 7 Hz), 6.80—8.95 (m, 10H)
4′-NH-i-Pr	35.7	Yellow powders (hexane-ethyl acetate); 165.7—168.5	1.17 (d, 6H, J = 6 Hz), 3.42—3.82 (1H, br), 5.92—8.12 (m, 10H)
4′-NMe$_2$	22.6	Orange needles (ethyl acetate); 203.2—205.1 (200)[b)]	3.13 (s, 6H), 6.70—8.41 (m, 10H)
4′-OMe	37.2	Yellow plates (ethanol); 150.0—151.3 (148)[c)]	4.03 (s, 3H), 6.80—8.50 (m, 10H)
3′,4′-(OMe)$_2$	27.8	Yellow prisms (ethyl acetate); 152.0—154.4	4.01 (s, 3H), 4.03 (s, 3H), 6.88—8.40 (m, 9H)
2′,4′-(OMe)$_2$	29.5	Yellow plates (ethyl acetate); 121.9—124.0 (124)[d)]	3.96 (s, 3H), 4.02 (s, 3H), 6.70—8.35 (m, 9H)
3′,4′,5′-(OMe)$_3$	27.0	Yellow needles (ethanol); 141.5—143.0 (135—136)[e)]	CDCl$_3$: 4.01 (s, 3H), 4.04 (s, 6H), 7.09—8.63 (m, 9H)
4′-Me	30.8	Yellow needles (ethyl acetate); 160—161.9 (162—163)[f)]	2.48 (s, 3H), 6.92—8.60 (m, 10H)
3′-Me	17.8	Yellow prisms (ethanol); 129.7—132.1	2.50 (s, 3H), 6.92—8.62 (m, 10H)
4′-H	32.8	Yellow plates (ethanol); 153.6—155.8 (153.0—155.0)[g)]	6.88—8.68 (m, 11H)
4′-Cl	18.8	Yellow needles (ethyl acetate); 156.2—158.1 (151)[h,i)]	Not measured
4′-Br	8.2	Yellow plates (ethanol); 136.2—137.9 (133)[h,i)]	Not measured
3′-Cl	8.1	Yellow plates (ethanol-hexane); 163.5—165.9 (170—171)[h,i)]	Not measured

a) Yields of pure crystals. b) Cited from Ref. 17. c) Cited from Ref. 18. d) Cited from Ref. 19. e) Cited from Ref. 20. f) Cited from Ref. 21. g) Cited from Ref. 22. h) Cited from Ref. 23. i) Cited from Ref. 24.

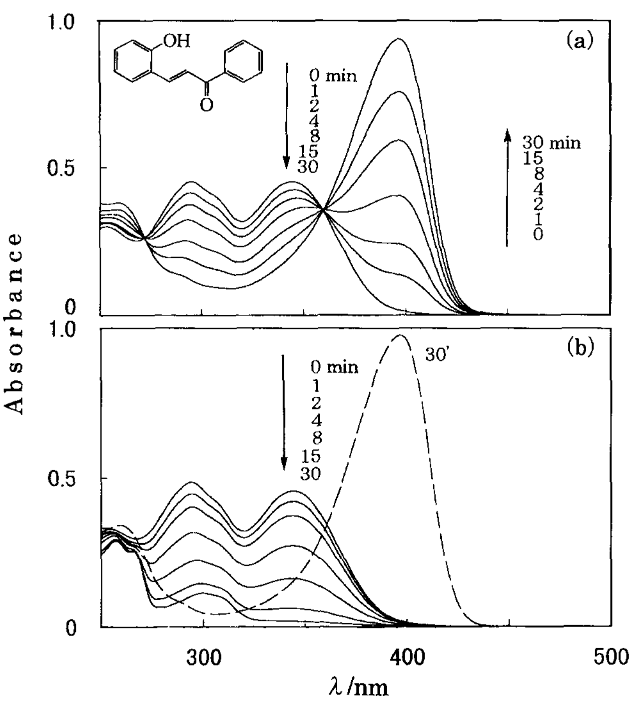


Fig. 1. Photochemical reactions of chalcone **1** in DME solution, (a) in the presence of 5 mM perchloric acid, (b) in the absence of acid, on irradiation with 365—366 nm light from a 100-W high-pressure mercury lamp. The broken curve in (b) refers to the spectral growth in the dark upon addition of 5 mM perchloric acid to the 30-min photolyzed neutral solution.

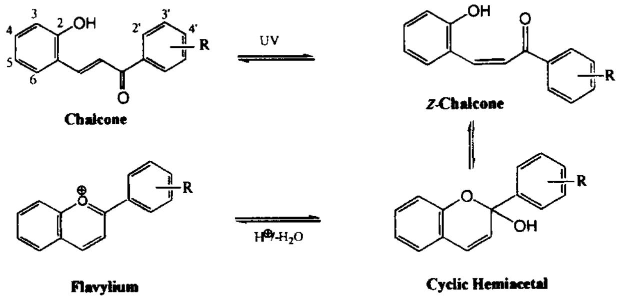
mated, assuming entire conversion of the chalcone into the flavylium ion. In the absence of acid (b), no flavylium band appears (solid curves) while absorption bands of chalcone **1** decrease with irradiation time. The 30-min irradiated PSS solution exhibits little absorption in the 280—400 nm region, implying that the photochemically formed Z-isomer has been substantially converted into the cyclic hemiacetal (2-hydroxy-2-phenyl-2H-1-benzopyrane) *in the absence of acid* (second step in the following Scheme 1). By the addition of perchloric acid (5 mM: 1 M = 1 mol dm^{-3}) to the PSS solution, acid-catalyzed dehydration of the hemiacetal takes place to give colored flavylium ion (broken curve in (b)). Similar results were obtained for the majority of chalcones listed in Table 2, excepting the amino-substituted chalcones (R = NMe$_2$, NH-i-Pr, NEt$_2$) which revealed some different features as described below. Table 2 summarizes the spectral features of a series of substituted 2-hydroxychalcones in DME in the absence and presence of 5 mM perchloric acid, before and after irradiation. All the chalcones listed in Table 2 were thermally stable in DME solution for several days in the presence or absence of 5 mM perchloric acid, and the colored (flavylium) solutions were stable at least for 24 h on standing in the dark at room temperature.

Figure 2(a) illustrates the spectral changes of 1-(4-dimethylaminophenyl)-3-(2-hydroxyphenyl)-2-propen-1-one (chalcone **5**) upon irradiation with 365—366 nm light in neutral tetrahydrofuran (THF) solution (solid curves), show-

Table 2. Absorption Spectra of 2-Hydroxychalcones in Neutral and Acid Solutions in 1,2-Dimethoxyethane (DME) before and after Irradiation with 365—366 nm Light[a)]

2-Hydroxychalcone	Neutral solution		Acid solution before irradiation		Acid solution after irradiation (flavylium ion)			
R	λ_{max}/nm	$\varepsilon_{max}/10^4\ M^{-1}\ cm^{-1}$	λ_{max}/nm	$\varepsilon_{max}/10^4\ M^{-1}\ cm^{-1}$	ISP/nm	λ_{max}/nm	A_{PSS}	$\varepsilon_{max}/10^4\ M^{-1}\ cm^{-1}$
4′-NEt_2	375	3.2	354	1.6	410	537	0.80	5.3
4′-NH-*i*-Pr	365	3.1	352	1.6	404	527	0.79	5.3
4′-NMe_2	369	3.0	353	1.5	408	536	0.76	5.0
4′-OMe	340	2.0	340	2.0	376	441	0.68	4.5
3′,4′-$(OMe)_2$	346	2.3	346	2.4	374	470	0.49	3.3
2′,4′-$(OMe)_2$	340	2.1	340	2.1	378	462	0.44	2.9
3′,4′,5′-$(OMe)_3$	345	2.0	345	2.0	382	461	0.40	2.7
4′-Me	343	1.7	343	1.6	365	410	1.18	3.9
3′-Me	343	1.6	344	1.6	361	400	0.99	3.3
4′-H	345	1.5	345	1.5	360	395	1.00	3.3
4′-Cl	348	1.6	348	1.6	365	403	1.09	3.6
4′-Br	348	1.6	349	1.6	366	406	1.11	3.7
3′-Cl	350	1.5	350	1.5	361	403	0.83	2.8

a) Chalcone was irradiated in 15—30 μM solution in DME in the presence of 5 mM perchloric acid under air. ISP refers to the isosbestic point appeared during the photoreactions, A_{pss} refers to the maximum absorbance of the flavylium ions formed in the photostationary state (PSS) solution, ε_{max}^{PSS} refers to approximate molar absorption coefficient estimated from A_{pss}.



Scheme 1.

ing photochemical *E*/*Z* isomerization. By addition of 5 mM perchloric acid to the PSS solution, the absorption band of the flavylium ion appears around 530 nm (broken curve). Under similar conditions, 2-methoxy derivative, i.e., 1-(4-dimethylaminophenyl)-3-(2-methoxyphenyl)-2-propen-1-one, undergoes efficient *E*/*Z* photoisomerization as shown in Fig. 2(b) (solid curves), but no flavylium ion is formed upon addition of 5 mM perchloric acid (broken curve). The spectra of the PSS solutions in (a) and (b) are quite similar to each other, implying that both the PSS solutions contain Z-isomers as the major species. This means that the Z-isomer of chalcone **5** is the most stable as such in neutral solution, but it undergoes acid-catalyzed conversion into cyclic hemiacetal upon addition of acid, followed by dehydration to flavylium ion. Other amino-substituted chalcones underwent similar reactions.

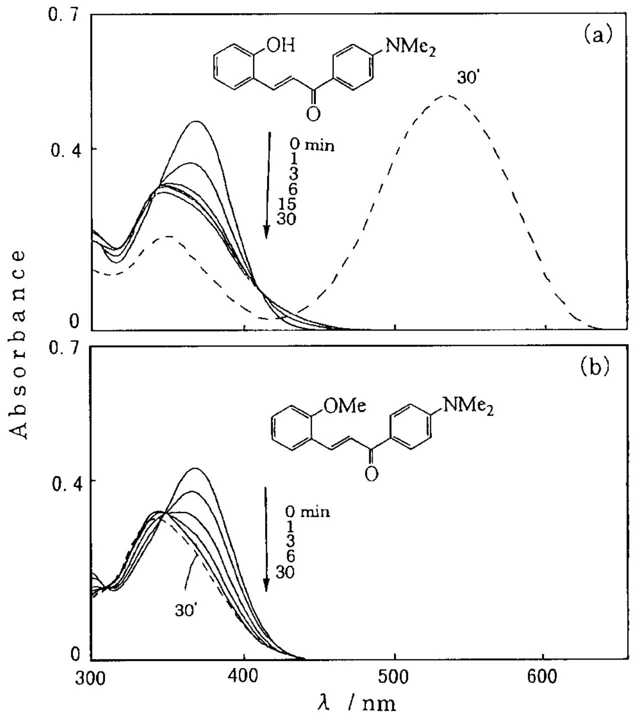


Fig. 2. Photochemical reactions of chalcone **5** (a) and its 2-methoxy derivative (b) in neutral THF solution (solid curves) on irradiation with 365—366 nm light. The broken curves refer to the spectra upon addition of 5 mM perchloric acid to the 30-min irradiated (PSS) solutions.

The quantum yields for the photochemical reactions were measured for chalcones with R = 4′-*H* (chalcone **1**), 4′-Cl (chalcone **2**), 4′-Me (chalcone **3**), 4′-OMe (chalcone **4**), and 4′-NMe_2 (chalcone **5**) in DME solution in the presence and absence of perchloric acid, by using the potassium tris(oxalato)ferrate(III) actinometer solution upon irradiation with monochromatic 365—366 nm light. As listed in Table 3, the quantum yields are high (around 0.34) in the acid solution and vary little with change in the substituent R, which are comparable to those obtained in the neutral solution. Further, the quantum yields in the acid solution are essentially constant towards the variation in the experimental conditions such as temperature, wavelength of light, and initial concentration of chalcone (Table 4), as well as the incident light intensity (0.33±0.03 against the variation in the intensity from 1.1×10^{-5} to 3.5×10^{-4} einstein $cm^{-2}\ min^{-1}$ at 365—366 nm). The constant features may be suitable for use as a chemical actinometer. However, exceptionally low values were obtained with chalcone **5** in the neutral solution

Table 3. Quantum Yields for the Formation of the Flavylium Ions in the Presence of Acid (ϕ_{FV}) and Consumption of Chalcones in the Absence of Acid (ϕ_{HC}), in 1,2-Dimethoxyethane (DME) Solution[a)]

Chalcone		Φ_{FV}	Φ_{HC}
No.	R	In the presence of acid	In the absence of acid
1	4′-H	0.34	0.36
2	4′-Cl	0.35	0.38
3	4′-Me	0.36	0.34
4	4′-OMe	0.36	0.31
5	4′-NMe$_2$	0.33	0.072

a) Initial chalcone concentrations were 0.2—0.3 mM, irradiated with 365—366 nm light beams.

Table 4. Effects of the Reaction Conditions on the Photochemical Quantum Yield of Chalcone **5** in DME in the Presence of 5 mM Perchloric Acid[a)]

Initial concn	Temperature	Irrad. wavelength	Quantum yield
mM	°C	nm	ϕ_{FV}
0.2	20	254	0.35
0.2	20	313	0.36
0.2	20	334	0.36
0.2	25	365—366	0.33
0.2	10	365—366	0.36
0.2	40	365—366	0.33
1.0	20	365—366	0.35
10.0	20	365—366	0.27
2.5	20	405	0.32

a) Dark reactions were negligible during the procedures.

(0.07 in DME, and 0.14 in toluene), for which no reasonable explanation can be offered yet.

Absorption spectra of the amino-substituted chalcones exhibit large hypsochromic shifts by the addition of acid, while other chalcones exhibit little changes (Table 2). Thus, Fig. 3 illustrates the spectral features of chalcone **5** in neutral DME solution (a), which is decreased by the addition of 5 mM *p*-toluenesulfonic acid (b), and much more decreased by the addition of 5 mM perchloric acid (c). The latter spectrum (c) is close to that of chalcone **2** with electron-withdrawing substituent (R = 4′-Cl). These results imply that the amino nitrogen atom is partially protonated by the addition of *p*-toluenesulfonic acid and almost entirely protonated by the stronger perchloric acid, according to the following equilibrium (Scheme 2):

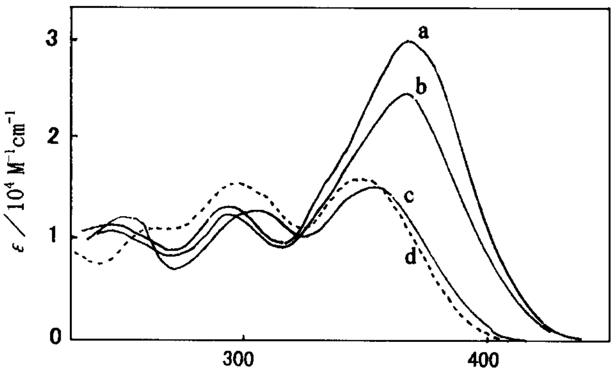
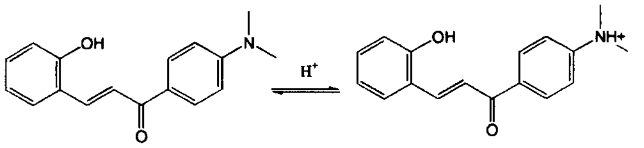


Fig. 3. Absorption spectra of chalcone **5** in DME solution, (a) in the absence of acid, (b) in the presence of 5 mM *p*-toluenesulfonic acid, (c) in the presence of 5 mM perchloric acid. Broken curve (d) refers to the spectrum of chalcone **2** (R_B = 4′-Cl) in DME solution in the absence of acid. Concentration of chalcone was 30 μM in each solution.



Scheme 2.

Since the quantum yield of chalcone **5** was significantly lower in the presence of *p*-toluenesulfonic acid (0.23)[12] as compared to the value around 0.34 in the presence of perchloric acid, it is assumed that the reactivity of the *Z*-chalcones (with R = NMe$_2$, NH-*i*-Pr, NEt$_2$) toward the thermal cyclization to 2-hydroxy-2-phenyl-2*H*-1-benzopyrane is governed by the protonation-deprotonation equilibrium: Thus, only the protonated forms of *Z*-chalcones are assumed to be reactive (comparable to *Z*-chalcone of **1** or **2**) while unprotonated forms are unreactive. In support for this assumption, the heats of formation calculated with the MOPAC-PM3 program under full structure optimization by using the COSMO method[25] (with a keyword "eps = 7.2" for 1,2-dimethoxyethane solution), implied that the unprotonated form of *Z*-chalcone **5** featured a high endothermicity by ca. 12 kcal mol^{-1} toward the cyclization process whereas *Z*-chalcone of **1** (as a protonated model for *Z*-chalcone **5**) featured a slight exothermicity by ca. −0.58 kcal mol^{-1}.

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