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Chemical actinometer with 2-hydroxy-4′-dimethylaminochalcone

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Abstract

The quantum yield of photochemical conversion of 2-hydroxy-4′-dimethylaminochalcone into 4′-dimethylaminoflavylium ion is approximately 0.23 in tetrahydrofuran solution in the presence of 5 mM *p*-toluenesulphonic acid on irradiation with UV light. The quantum yield is essentially constant as a function of the reaction conditions, such as the reaction time, temperature, substrate concentration and light intensity, but the absorption spectra of the reactant and product are well separated. These features are favourable for use as a chemical actinometer.

Keywords: Chemical actinometer; 2-Hydroxychalcone; Quantum yield

1. Introduction

The photochemical reactions of the methoxylated and hydroxylated derivatives of 2-hydroxychalcone have been studied previously by Jurd [1] and Dewar and Sutherland [2], and the thermal interconversions of 2-hydroxychalcones and flavylium ions have been extensively studied by Bruoillard et al. [3–5] and McClelland and coworkers [6,7]. In an attempt to develop a new photochromic system of 2-hydroxychalcones and flavylium ions, we investigated the effects of the substrate structure and medium conditions and related mechanisms [8].

In this paper, we investigate the photochemical conversion of 2-hydroxy-4′-dimethylaminochalcone (chalcone **1**; Fig. 1) into 4′-dimethylaminoflavylium ion (flavylium **2**; Fig. 1), and its application as a rapid and convenient chemical actinometer. The quantum yield of the photoreaction is practically independent of the reaction conditions, and the UV–visible absorption spectra are favourable for spectroscopic measurements.

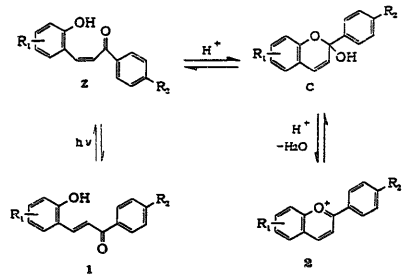

Fig. 1. Photochemical colouration of chalcone **1** and thermal decolouration of flavylium ion **2** ($R_1 \equiv H$ and $R_2 \equiv N(CH_3)_2$).

2. Experimental details

The UV–visible absorption spectra were recorded on a Hitachi 150-20 spectrophotometer; proton nuclear magnetic resonance (^1H NMR) spectra were obtained on a Hitachi R-24 spectrometer. The pH value of the solution was measured with a Yanaco PH-7 pH meter. The UV irradiation apparatus was a Hitachi 204 fluorescence spectrometer, which provided monochromatic light beams from a 120 W high-pressure mercury lamp. The quantum yield was measured using the potassium ferrioxalate actinometer [9], by the method of "total absorption" of incident light [10], by adjusting the substrate concentration so that the absorbance of the incident light was no less than 2.0.

Solvents were distilled before use unless otherwise noted. 2-Hydroxy-4′-dimethylaminochalcone (**1**) was prepared as follows. To a 100 ml ethanol solution containing salicylaldehyde (20 g, 0.16 mol) and sodium hydroxide (41 g) was added a 300 ml ethanol solution of 4-dimethylaminoacetophenone (26.7 g, 0.16 mol) slowly with vigorous stirring.

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The reaction mixture was stirred for 4 days at room temperature. On neutralization with aqueous acetic acid, the precipitates were separated on filter paper (25.6 g, 58.4% yield). Crystallization from ethanol gave orange needles of **1**: m.p. 194.0–195.5 °C. ^{1}H NMR δ (ppm) (60 MHz, dimethylsulphoxide-d_6): 3.0 (s, 6H), 6.6–8.1 (m, 10H), 10.2 (s, 1H). 4′-Dimethylaminoflavylium perchlorate (**2**) was prepared by acid-catalysed condensation from salicylaldehyde and 4-dimethylaminoacetophenone in 70% yield according to the reported method [11].

3. Results and discussion

3.1. Medium conditions and reactivities

Table 1 compares the quantum yield of photochemical conversion of chalcone to flavylium in different medium conditions on irradiation with 365–366 nm light, showing strong medium effects. The quantum yield is relatively high in tetrahydrofuran (THF) and tert-butyl alcohol in the presence of added acid. The acid is necessary for the acid-catalysed thermal reaction of the *cis*-chalcone (Z) into a cyclic acetal (C) as shown in Fig. 1.

Fig. 2(a) illustrates the spectral changes of chalcone in acidic THF solution on irradiation with 365–366 nm light. The effects of dissolved oxygen were practically negligible. The coloured solution at the photostationary state exhibits strong absorption in the visible region (well separated from the chalcone band) and weak absorption in the shorter wavelength region below 420 nm. The latter feature is suitable for the selective photoexcitation of chalcone, whereas the former feature permits sensitive and accurate spectroscopic measurements. The coloured solution undergoes substantial thermal bleaching on heating as shown in Fig. 2(b), but is fairly stable at room temperature in the dark as well as in visible light of λ > 450 nm. The absorption spectrum of the bleached solution is different from that of chalcone. Therefore the photochemical colouration followed by thermal bleaching is not a reversible process under these medium conditions, but is reversible under other medium conditions. The medium effects and related mechanisms are still under investigation [12,13].

Table 1
Variation in the quantum yield of chalcone **1** with the medium conditions [a]

Solvent	Added acid (or pH)	Quantum yield [b]
tert-Butyl alcohol	Sulphuric acid (5 mM)	0.14
Ethanol	Sulphuric acid (5 mM)	0.05
Methanol	Sulphuric acid (5 mM)	0.01
Tetrahydrofuran	*p*-Toluenesulphonic acid (5 mM)	0.22
Ethyl acetate	Acetic acid (10 wt.%)	0.06
Aqueous ethanol (1:1)	pH 4	0.002
Aqueous ethanol (1:9)	pH 4	0.023

[a] Solution of chalcone (0.075 mM) was irradiated with 365–366 nm light without deaeration. Adjustment of pH in aqueous ethanol solution was carried out with dilute aqueous sodium acetate and sulphuric acid solutions.
[b] Potassium ferrioxalate actinometer was used [9].

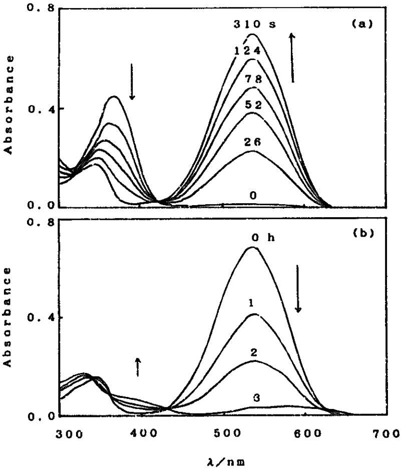

Fig. 2. (a) Photochemical colouration of chalcone **1** (0.015 mM) in tetrahydrofuran solution in the presence of added *p*-toluenesulphonic acid (5 mM) on irradiation with 365–366 nm light. The solution was degassed by bubbling with pure nitrogen for 30 min before irradiation and kept air tight in a reaction tube during irradiation. Similar results were obtained in solution without deaeration. (b) Thermal decolouration of the coloured solution (flavylium **2**) on heating at 50 °C.

3.2. Quantum yields under different conditions

Fig. 3 illustrates the linear response of the photoreaction of chalcone vs. the irradiation time with 365–366 nm light in THF solution in the presence of 5 mM *p*-toluenesulphonic acid. For the lowest concentration range of chalcone (0.075 mM), the absorbances of the solutions at 365 nm before and after 20 min of irradiation are 2.2 and 2.1 respectively, i.e. total absorbance of the incident light. Similarly, the absorbances at 365 nm of the actinometer solution before and after 10 min of irradiation are larger than 3. No significant effects of dissolved oxygen were found, and hence the reactions were carried out without deoxygenation.

Table 2 illustrates the variation in the quantum yield (at 365–366 nm) as a function of the change in the concentration of *p*-toluenesulphonic acid and the water content in THF solution. The results imply that a feasible range of *p*-toluenesulphonic acid concentration is 5 ± 2 mM, whereas contamination with water should be less than approximately 0.5%. Under these conditions, the approximate range of error in the quantum yield is assumed to be ±0.01.

As shown in Table 3, the quantum yield is practically constant as a function of the change in the initial concentration

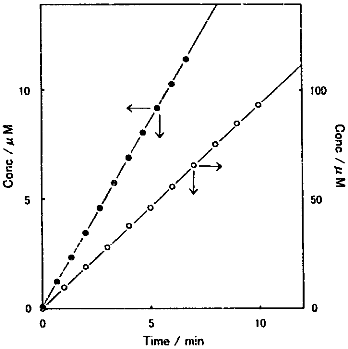

Fig. 3. Relative rates of the photochemical reactions of chalcone **1** in THF solution in the presence of 5 mM *p*-toluenesulphonic acid (●) and the potassium ferrioxalate actinometer (○) on irradiation with 365–366 nm light without deaeration. Similar results were obtained for the photoreaction of chalcone **1** in deaerated solution.

Table 2
Influence of *p*-toluenesulphonic acid and water contents on the quantum yield of chalcone **1** [a]

Water added (wt.%)	*p*-Toluenesulphonic acid (mM)	Quantum yield
0 [b]	2	0.22
0 [b]	5	0.23
0 [b]	7	0.23
0.4	5	0.21
2	5	0.17
5	5	0.13

[a] Irradiated with 365–366 nm light in tetrahydrofuran (THF) solution.

[b] Fresh THF of Wako's guaranteed grade (assay minimum, 99.5%) was used as received.

of chalcone and the reaction temperature, although it varies with the irradiation wavelength (particularly at 254 nm). In addition, the quantum yield is constant vs. the intensity of the incident light at 365–366 nm (data not shown). These features are suitable for application as a chemical actinometer.

Table 3
Effect of the reaction conditions on the photoreaction quantum yield of chalcone **1** in acidic THF solution [a]

UV light λ (nm)	Initial concentration of chalcone (mM) [b]	Temperature (°C)	Quantum yield [c]
365–366	0.075	10	0.23
	0.075	20	0.23
	0.075	30	0.22
	0.15	20	0.24
	0.30	20	0.23
	1.0	20	0.24
	10.0	20	0.23
334	0.15	20	0.21
313	0.30	20	0.23
254	0.25	20	0.16

[a] In THF solution containing 5 mM *p*-toluenesulphonic acid.

[b] Under these conditions, the incident light was entirely (more than 99%) absorbed by chalcone.

[c] Quantum yields estimated on the basis of the potassium ferrioxalate actinometer [9]. Approximate range of error is estimated to be ±0.01.

Table 4
Thermal stabilities of chalcone **1** and flavylium **2** in acidic THF solution [a]

Chalcone **1** (10 mM)		Flavylium **2** (0.15 mM)	
Time (h)	Flavylium formed (%)	Time (min)	Flavylium retained (%)
0	0.01	0	100
8	0.02	10	99
24	0.03	20	99
54	0.02	30	99
77	0.02	60	99

[a] In THF solution containing 5 mM *p*-toluenesulphonic acid at room temperature in the dark.

3.3. Stabilities of the chalcone and flavylium solutions in the dark

A solution of chalcone **1** in acidic THF is thermally stable, and no significant colouration is observed on standing in the dark at room temperature for several days as shown in Table 4 (thus permitting long-time storage at a high concentration). Although the natural anthocyanin pigments are stabilized by complex copigmentation and/or association [14,15], their aglycones (flavylium ions) are subject to rapid thermal bleaching in aqueous solution. Thus the hydroxylated and alkoxylated derivatives of flavylium ions generally undergo rapid decolouration into 2-hydroxychalcones in weak acid solution at pH > 3 [3–7,16]. In contrast, 4′-amino-substituted flavylium ions are much more stable: the photolysed (coloured) solution is stable up to pH 5 in aqueous solution. The present system is superior, as a chemical actinometer, to our previous actinometer system with 2-hydroxy-4′-methoxychalcone [17] in that the former is more thermostable and can be stored for a long time in the dark. Further investigation to cover the visible region from 405 to 436 nm is in progress.

4. Conclusions

A solution of 2-hydroxy-4′-dimethylaminochalcone in tetrahydrofuran in the presence of added acid is suitable as a chemical actinometer in the UV region (254–366 nm). The quantum yield of around 0.23 is essentially constant as a function of changes in the reaction conditions, such as the substrate concentration, reaction time, temperature and light intensity. The absorption spectra of the reactant (chalcone) and product (flavylium) are well separated, and favourable for easy and accurate measurements. The chalcone is easily (in one step) prepared in a good yield (approximately 60%) from cheap commercial chemicals.

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