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Photochromic Properties of 2-Hydroxychalcones

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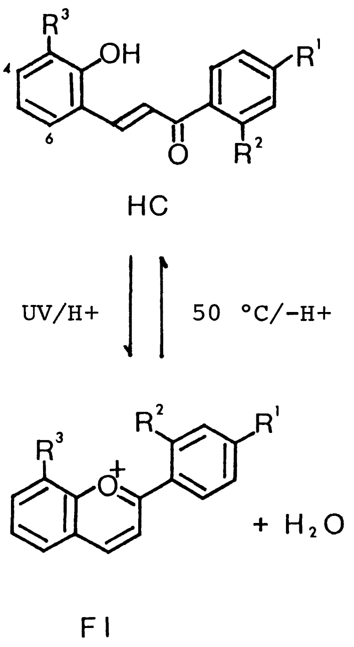
Photochemical and thermal interconversions between 2-hydroxychalcones (λ_{max} 330-360 nm) and flavylium ions (400-460 nm) have been studied in dilute aqueous ethanol solutions. The reactions were fairly clean and recyclizable, though varied with substituents and pH. The quantum yields for photochemical coloration were about 0.1 or less.

2-Hydroxychalcones (HC) are photochemically converted into colored flavylium ions (FI) in acid solutions, via photochemical E/Z isomerization followed by acid-catalyzed intramolecular cyclization and dehydration.[1,2] Thermal stabilities of HC and FI are highly sensitive to the acidity of solution and the substituents. If HC and FI are thermodynamically or kinetically stable in the dark and photochemically interconvertible, they may constitute a new type of photochromic system. However, HC with hydroxyl or alkoxyl groups at the 4- and/or 6-positions, which have been most extensively studied in relation to the naturally occurring anthocyanines and derivatives, are generally unstable and in rapid equilibrium with FI in acid solution in the dark.[1,3,4] Contrary, in the absence of strong electron-donating groups at these positions, both HC and FI forms are stable in acid solution in the dark at room temperature. In spite of the considerable studies on the spectroscopic and photochemical properties[1-3] as well as thermal equilibria of the HC-FI systems,[3,4] no systematic studies on potential photochromic properties have been found, nor been reported the quantum efficiencies and the recyclizabilities for the coloration-discoloration interconversions. In this letter we report some preliminary work on the photochromic and/or thermochromic properties of the HC-FI systems in solution, including the effects of substituents and pH.

A dilute solution (10^{-4} mol/dm^3) of <u>1</u> (HC: R^1=MeO, R^2=R^3=H) underwent photochemical coloration on UV irradiation under acidic conditions in aqueous ethanol (1:1 in volume). A photostationary state (pss) was attained in ca. 20 min, hereafter no significant increase in the absorbance of visible band was observed on further irradiation. The quantum yield for coloration, ϕ, was 0.12 with 313-334 nm light. The colored solution was stable at room temperature in the presence or absence of visible light, but underwent substantial discoloration on heating as shown in Fig. 1. Clear isosbestic points were observed at 387 and 282 nm. Figure 1 illustrates the reversibility of <u>1</u> for the coloration-discoloration cycles, showing rather low recyclizability.

The quantum yields with 2 (R^1=R^2=MeO, R^3=H) and 3 (R^1=R^3=MeO, R^2=H) were 0.08 and 0.02, respectively. Other HC (R^1=dimethylamino group) as well as heterocyclic analogs with furyl and thienyl rings showed similar photochemical responces. The photochromic properties of HC varied also with the acidity of solution. Thus, the absorption maxima of the colored form of 1 at pss, relative rates for photochemical coloration (%/min), and relative rates for thermal discoloration (%/h), which were estimated from the absorption spectra on the assumption that the absorption coefficients of the colored and/or uncolored forms remain constant in the pH region of 1-4, varied with pH as follows: 0.70, 6.5, 4.8 at pH 1.5; 0.52, 6.9, 25.4 at pH 2.2; 0.18, 2.72, 56.7 at pH 3.2; 0.03, 0.42, 69.2 at pH 4.2.

The present photochromic systems may be compared with those of H-transfer tautomerism,$^{5)}$ and have several characteristics: they operate in aqueous solution at room temperature; the reactions can be regulated by pH; and the reactions do not essentially suffer from the dissolved oxygen.



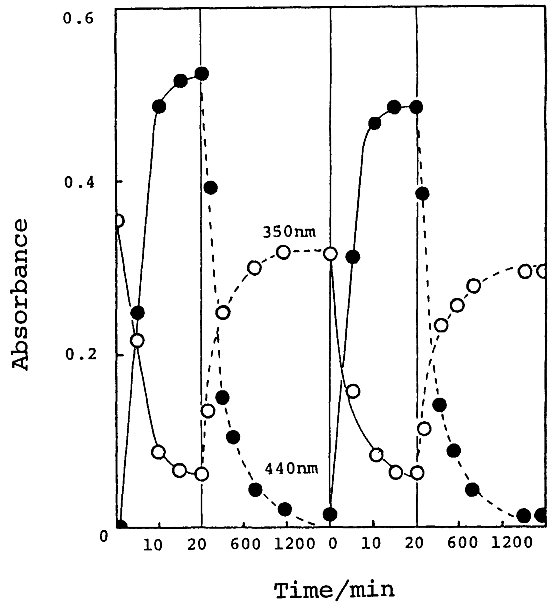


Fig. 1. Coloration (solid line) and discoloration (broken line) of 1 at pH 2.4.

References

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