Electronic Supplementary Material (ESI) for New Journal of Chemistry

Effect of *β*-cyclodextrin in the chemistry of 3',4',7-trihydroxyflavylium

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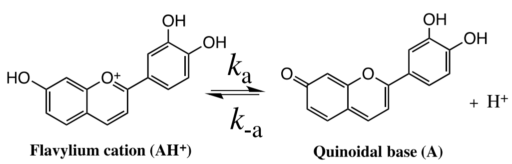
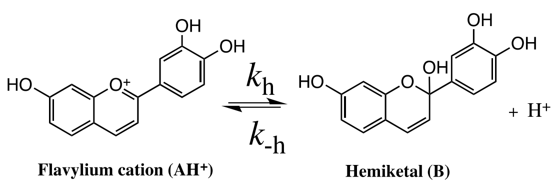
Demonstration of eq.(1) of the manuscript

The flavylium cation is stable only at very acidic pH values. Raising the pH a sequence of chemical reactions take place as follows:



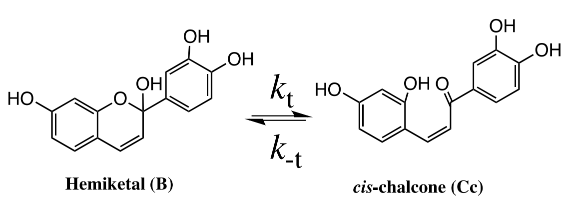
Proton Transfer (A1)

The quinoidal base is formed by proton transfer, eq.(A1). This reaction is by far the fast of the network.



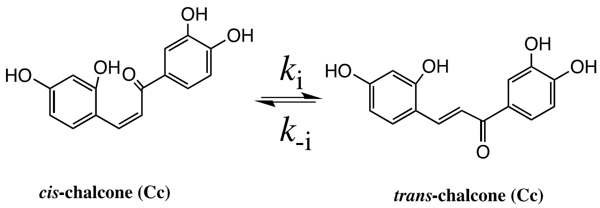
Hydration (A2)

In competition with eq.(A1) the flavylium cation can hydrate in position 2 to give the hemiketal, eq.(A2). On the other hand, the hemiketal leads to the *cis*-chalcone upon opening of the ring, by a tautomeric process, eq.(A3)



Tautomerization (A3)

Finally, the *trans*-chalcone is formed from the isomerization of the *cis*-chalcone, eq.(A4)



Isomerization (A4)

In eqs.(A1) to (A4) the equilibrium constants are defined by $K_n = \frac{k_n}{k_{-n}} \quad n = a, t, i$

The mass balance gives in acid to moderately acid solutions is given by eq.(A5)

$$C_0 = [AH^+] + [A] + [B] + [Cc] + [Ct] = [AH^+] + [CB] \qquad \text{(A5)}$$

Where [CB]=[A]+[B]+[Cc]+[Ct]

Using eqs.(A1) to (A4)

$$C_0 = [AH^+] + \frac{K_a}{[H^+]}[AH^+] + \frac{K_h}{[H^+]}[AH^+] + \frac{K_h K_t}{[H^+]}[AH^+] + \frac{K_h K_t K_i}{[H^+]}[AH^+] \qquad \text{(A6)}$$

Defining $K_a^{'} = K_a + K_h + K_h K_t + K_h K_t K_i$ (A7)

$$C_0 = [AH^+](1 + \frac{K_a^{'}}{[H^+]}) \qquad \text{(A8)}$$

Defining the mole fraction of the flavylium cation

$$X_{AH+} = \frac{[AH^+]}{C_0} = \frac{[H^+]}{[H^+] + K_a^{'}} \qquad \text{(A9)}$$

and the mole fraction of the remaining species

$$X_{CB} = \frac{K_a^{'}}{[H^+] + K_a^{'}}$$

This is equivalent to a single acid base equilibrium between AH^+ and a "base" CB

$\mathbf{AH^+} + H_2O \rightleftharpoons \mathbf{CB} + H_3O^+$ $\qquad K'_a = K_a + K_h + K_h K_t + K_h K_t K_i$ (A10)