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On the photosensitized formation of $^1O_2$ (^{1} $_2$) by flavonoids

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The quantum yields of the photosensitized formation of singlet molecular oxygen from luminescence experiments in benzene solutions of 3,5,7,3′,4′-pentamethoxyflavone, 3-hydroxy-5,7,3′,4′-tetramethoxyflavone and 5-hydroxy-3,7,3′,4′-tetramethoxyflavone were found to be 0.49±0.05 and $< 10^{-2}$, respectively.

Flavonoids play an important role in biochemical processes.[1] Therefore, the photochemical properties of these molecules are of interest in the study of light-induced biochemical processes which are not well understood. Here we focus on the photoactivation of molecular oxygen by flavonols.

Singlet molecular oxygen ($^1O_2$) is a key intermediate in many photobiochemical reactions. From experiments on the photoformation of $^1O_2$ by quercetin, it has been deduced that the quantum yield of $^1O_2$ is less than 10^{-3}.[2] This fact was interpreted in terms of intramolecular hydrogen bonding. With the ultimate aim of further understanding the role of the C-5 and C-3 hydroxy groups in this process, we present the quantum yield of $^1O_2$ observed in the solutions of quercetin derivatives.

The substrate molecules employed were 3,5,7,3′,4′-pentamethoxyflavone **1**, 3-hydroxy-5,7,3′,4′-tetramethoxyflavone **2** and 5-hydroxy-3,7,3′,4′-tetramethoxyflavone **3**. Compounds **1**–**3** were preparated by methylation of quercetin and rutin by standard methods and the authenticity of the samples were confirmed by UV spectroscopy.[3] Benzene and [$^2H_6$]benzene were used as solvents. Near-infrared time-resolved luminescence was used as a diagnostic means for the analysis of the $^1O_2$ formation.[4]

The excitation of flavonoids yields dramatically different results. Photosensitized luminescence from the ^{1} $_2$-state of O^2 in solutions of **1** was observed. In contrast to **1**, the light-induced formation of $^1O_2$ by **2** and **3** was not observed. The luminescence intensity in solutions of **1** were measured as a function of the delay time. The decay rate constant k is determined from the following equation (1),

$$I_t = I_0 e^{-kt} \qquad (1)$$

where I_t is the observed intensity at time t after excitation, I_0 is the intensity at zero delay time, t is the delay time, k is the decay rate constant.

One can see that value of k depends on the concentration of **1** in [$^2H_6$]benzene solutions: concentration/mol dm^{-3} (k/s^{-1}) 9.94×10^{-5} (1.86×10^3), 6.1×10^{-5} (1.76×10^3), 4.35×10^{-5} (1.56×10^3), 2.52×10^{-5} (1.6×10^3). The differences in decay rate observed for different concentrations of **1** might be simply due to the quenching of $^1O_2$. A linear least-squares extrapolation of the cancentration dependence of k yielded an intercept of 1.46×10^3 s^{-1}, from which ($k = 1/\tau$) a limiting lifetime of $(684\pm50)\times10^{-6}$ s was calculated (for benzene the τ value of 29.5×10^{-6} s was obtained). This plot has a slope of $(4.0\pm1.0)\times10^6$ dm^3 mol^{-1} s^{-1}, corresponding to the total quenching rate constant of $^1O_2$ by **1** according to the Stern-Volmer equation

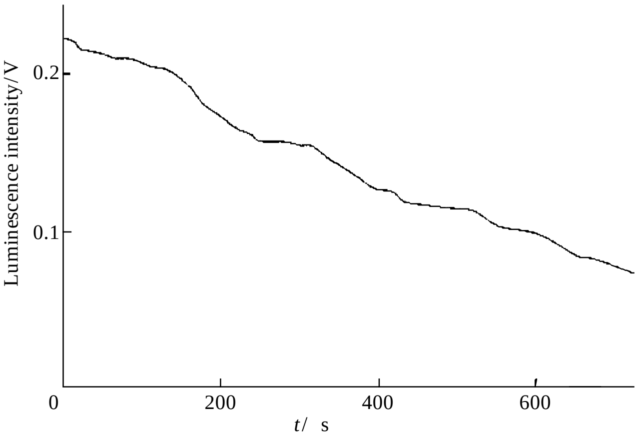

Figure 1 Time-dependence luminescence intensity of $^1O_2$ (^{1} $_g$) in [$^2H_6$]benzene solution of 3,5,7,3′,4′-pentamethoxyflavone ($c = 4\times10^{-5}$ M).

$$k = k_0 + k_Q[\mathrm{Qu}] \qquad (2)$$

Here k_Q is the quenching rate constants, [Qu] is the concentration of **1**. The rate constants of the $^1O_2$ quenching by **2** and **3**, estimated from experiments on the quenching of the photosensitized luminescence of $^1O_2$ by anthracene in [$^2H_6$]benzene solutions, are 2.0×10^6 and 2.5×10^6 dm^3 mol^{-1} s^{-1} respectively.

For the quantum yield of $^1O_2$ we have[5]

$$\gamma = \varphi/k_r\tau, \qquad (3)$$

where k_r is the rate constant of the radiative channel, τ is the lifetime of $^1O_2$ in solution, and φ is the luminescence quantum yield expressed as

$$\varphi = \frac{I_0}{I_{\mathrm{exc}}(1-10^{-A})} \qquad (4)$$

I_0 is the initial luminescence intensity obtained by extrapolation of I_t to $t = 0$, I_{exc} is the excitation light intensity, and A is the absorbance density at the excitation wave-length.

Quantum yields of $^1O_2$ in solutions of **1**–**3** were determined by relative methods using a benzene solution of Pd-mesoporphyrin-IX dimethyl ester ($\gamma^{\mathrm{std}} = 1.0$)[6] as standard. A 10 mm square cell was used for luminescence measurements with solution optical density $A = 0.70$ at 337nm. Assuming that $I_{\mathrm{exc}}(1-10^{-A})$ parameter is constant, the ratio of γ in the solutions of both sensitizers is given by

$$\gamma = \gamma^{\mathrm{std}} \frac{I_0}{I_0^{\mathrm{std}}} \qquad (5)$$

The result for **1** is $\gamma = 0.49\pm0.05$ in benzene. The γ values for **2** and **3** are substantially less than 10^{-2}.

One can see that the rate constant for the quenching of $^1O_2$ by **1** is relatively low. This compound is similar in this respect to **2** and **3**. However, the quantum yield of $^1O_2$ in a solution of **1** is higher than the observed value γ for **2** and **3**. We associate these differences with the photophysical properties of flavones.

It is well-known that the energy of $^1O_2$ is 22.5 kcal mol^{-1} (1 cal = 4.184J).[2,6] Spectroscopic studies[7] suggest that the triplet state energy of singlet–triplet separation for **1** are 56 and 19 kcal mol^{-1}, respectively. Similar data are predicted for the other flavonols.[2] This is evidence that $^1O_2$ can be sensitized by energy transfer from the triplet state of flavones to $^1O_2$ (^{3} $_g^-$). Experimentally, γ for **2** was found to be less than that for **1**. This is due to the specific intramolecular interactions between the proton of the hydroxide group at the C-3 position with the

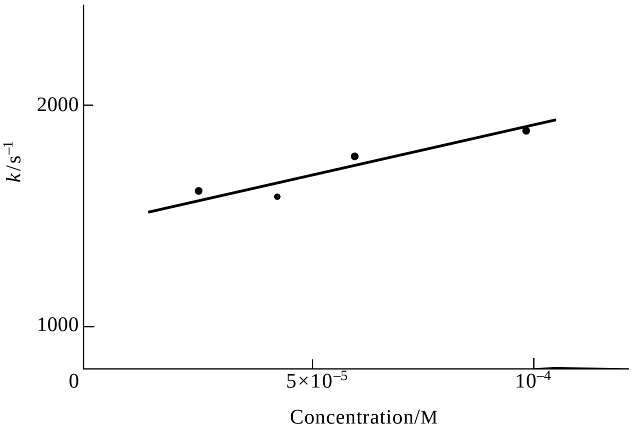

Figure 2 Dependence of the rate constant for the luminescence decay of $^{1}O_2$ (^{1} $_{g}$) on the concentration of 3,5,7,3′,4′-pentamethoxyflavone.

carbonyl oxygen in the excited state of **2**.[8] It is important to note that this process leads to a decrease of the triplet state population of **2**.[2] The experimental results show that the hydroxide group at the C-5 position leads to a similar effect. Consequently the OH group at the C-5 position also plays a key role in the excited state deactivation of **3**. For **3** H-transfer also quenches the excited states.

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