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Combined experimental and theoretical study of the photochemistry of 4- and 3-hydroxycoumarin

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ABSTRACT

Steady-state and time-resolved optical spectroscopy techniques were employed to study the photo-physics and photochemistry of 4- (4HC) and 3-hydroxycoumarin (3HC). We found that the pK_a of 4HC in aqueous solutions is about 7.5 and the pK_a^* is only 4.5. We also found that the nonradiative rate of 4-hydroxycoumarin is high and the excited state proton transfer (ESPT) rate to water is rather slow and so an ESPT process is not observed. Quantum mechanical calculations confirm that the ESPT rate should be slow and the intersystem crossing rate $S_1 \rightarrow T$ is large. An ESPT process was also not observed for 3HC, but it might still take place and not being observed as the fluorescence quantum yield of the anion is two orders of magnitude smaller than that of the protonated form. The nonradiative decay of protonated 3HC is explained with an H-atom abstraction mechanism, leading to the formation of a radical species.

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1. Introduction

Photoacids are hydroxyaryl compounds with weak acidity in their ground state, whereas in their first excited electronic state they are much stronger acids [1–15]. Usually their excited-state pK_a^* is lower by 7–10 pK_a units. For weak photoacids with $3 > pK_a^* > 0$ the logarithm of the excited state proton transfer rate constant $\log_{10}(k_{PT})$ scales close to linearly with their pK_a^* . For $pK_a^* \approx 3$ the ESPT to water rate constant k_{PT} is about $5 \times 10^7 \text{ s}^{-1}$ and for $pK_a^* = 0$ $k_{PT} \approx 5 \times 10^{10} \text{ s}^{-1}$.

Bifunctional compounds possess both photoacidic and photo-basic functional groups in close proximity. These compounds may undergo in the excited state both excited-state proton transfer from the acidic group and protonation of the photobase group. 7 and 8 hydroxy-quinolines were studied by several groups [15–19] and are good examples of bifunctional compounds with both photoacidic and photobasic groups on the same compound in close proximity. The direct proton transfer reaction between the photoacidic and the photobasic sites may occur via a solvent bridge consisting of two or three protic solvent molecules. It was found experimentally that both 7 and 8-hydroxyquinolines form

the zwitterion upon photoexcitation at an ultrafast rate. Sebastini and coworkers¹⁶ calculated for 7-hydroxyquinoline the formation of a zwitterion in the excited state. They found that the energy potential of the reaction paths indicates that the proton transfer mechanism occurs in a concerted fashion, since no stable intermediates are formed along the water wire. A similar reaction occurs between a photoacid and a weak base introduced in aqueous solutions. Mohammed et al. [17] using femtosecond transient IR technique studied the photoprolytic processes of HPTS in concentrated sodium acetate D_2O solutions. They concluded that proton transfer to the acetate anion proceeds by a proton hopping mechanism through water bridges that consists of one to five water molecules and also directly to the acetate.

7-hydroxycoumarin (also known as umbelliferon or Umb for short, here we refer to it also as 7HC) is a weak acid in the ground state [20] with a $pK_a \approx 7.8$ and a photoacid with $pK_a^* \approx 0.4$. The excited state proton transfer (ESPT) rate constant in water is $k_{PT} \approx 2 \times 10^{10} \text{ s}^{-1}$ ($\tau_{PT} = 50 \text{ ps}$). In methanol the ESPT rate of Umb is smaller by a factor of about 70 and is estimated to be $\sim 3 \times 10^8 \text{ s}^{-1}$.

In the ground-state 7HC in aqueous solutions of $pH > 0$ exists in two forms: N (OROH) and A(OR⁻). The tautomeric T form is not observed in the ground state, whereas in the excited state 7-hydroxycoumarins spectroscopy shows that the zwitterion T form also exists. The major photoprolytic process in aqueous solution is an ESPT to reach the A form and to a lesser extent the T species is formed by a step-wise mechanism.

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In a previous paper we have suggested that the photoacidity of 7-hydroxycoumarin is used by plants in order to resist fungal and bacterial infections [21]. 3-hydroxycoumarin, as well as unsubstituted coumarin, provided photoprotection from UVB-induced embryotoxicity to sea urchin gametes and embryonic cells [22]. This photoprotection was only provided when the coumarins were added to cells prior to UVB irradiation. By their turn, other coumarins, as 4- and 7-hydroxycoumarins, did not provide any photoprotection [22]. In the current work we study the photo-physics and photochemistry of 4- and 3-hydroxycoumarin, shown in Scheme 1 along with 7-hydroxycoumarin.

The absorption and steady-state fluorescence of 4-hydroxycoumarin was studied previously by several groups [23–25]. We use steady-state and time-resolved fluorescence techniques, and quantum mechanical calculations in order to study the photo-physics and photochemistry of both 4- (4HC) and 3-hydroxycoumarin (3HC). Scheme 2 shows the possible forms of 4HC, which can also be attributed to 3HC.

2. Materials and methods

2.1. Experimental methods

4HC and 3HC were purchased from Sigma-Aldrich and no further purification was carried out in our experiments. We used fresh solutions of this compound in all measurements. Solvents of HPLC grade or analytical grade were used in this study. All solvents were purchased from Sigma-Aldrich.

For the time-correlated single-photon-counting (TCSPC) measurements, we used, for sample excitation, a cavity-dumped titanium:sapphire femtosecond laser (Mira, Coherent). The laser output consists of 120 fs pulses over the spectral range of 760–860 nm. The third harmonic of the laser was used to excite the samples. The cavity dumper operated at a rate of ~ 800 kHz. The TCSPC detection system was based on a Hamamatsu 3809U multichannel-plate photomultiplier and an Edinburgh Instruments TCC 900 integrated TCSPC system. The time response of the instrument was approximately 40 ps (full-width at half-maximum, FWHM). The excitation-pulse energy was reduced by neutral-density filters to about 10 pJ.

The steady-state emission and absorption spectra were recorded by a Horiba Jobin Yvon FluoroMax-3 spectrofluorometer and a Cary 5000 spectrometer.

2.2. Quantum mechanical methods

The calculations were carried out by employing the Gaussian 09 program package [26]. The ω B97XD functional and the 6–31G(d,p) basis set were used to obtain the ground-state (S_0) geometries of 4HC and 3HC [27], which were characterized as minima or transition states in their potential-energy surfaces (PES) by subsequent vibrational-frequency calculations.

The PT reactions were modeled by performing an intrinsic-reaction-coordinate (IRC) calculation, in which the transition state

is connected to the reactants and products [28]. These calculations were also performed at the ω B97XD/6–31G(d,p) level of theory, while the S_0 PES was re-evaluated by performing single-point energy calculations at the ω B97XD/6–31+G(d,p) level of theory. The excited-state PES was obtained in a similar manner, by calculating the respective Franck-Condon curves. Such curves can be constructed by obtaining the time-dependent (TD) ω B97XD/6–31+G(d,p) vertical-excitation energies at the respective S_0 structures. Such alternative strategy arises from the difficulty in theoretically following an ESPT reaction in the excited state. The choice of an effective reaction coordinate is far from trivial, as the motion of the proton is accompanied by a significant electronic rearrangement. It is normally coupled to other degrees of freedom and is associated with problems related to classical or quantum treatment of its dynamics [29–31]. Moreover, the inability to analytically resolve second derivatives of excited-state energy severely impairs the modelling of ESPT reactions entirely on the excited state. The construction of the Franck-Condon curves is also validated by the notion that the absorption spectrum often reflects the main features of the emissive state, differing only by a red shift that occurs as a result of geometrical relaxation of the molecule [32–34] and so, this approach has been used routinely with good results in the study of ESPT reactions [35–43].

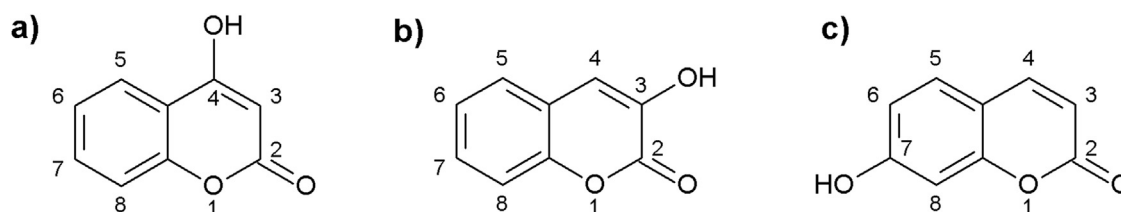
The involvement of triplet states was also studied by constructing Franck-Condon curves, in which the PES of T_1 and higher triplet states were modelled by single-point calculations (at the ω B97XD/6–31+G(d,p) and TD- ω B97XD/6–31+G(d,p) levels of theory) on S_0 structures. All optimization, frequency and IRC calculations were performed *in vacuo*, while all single-point calculations were made in implicit water, which was modelled by the use of the conductor-like polarizable-continuum model (CPCM) for 4HC [44], and the SMD model for 3HC [45]. ω B97XD is a long-range-corrected functional and was chosen because of good results in local $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, charge-transfer and Rydberg states [46]. Another advantage of this functional is that it includes an empirical dispersion-correction term, which may be important for correctly modelling these ESPT reactions.

3. Results and discussion

3.1. Steady-state spectra of 4- and 3-hydroxycoumarin

Fig. 1 shows the absorption spectra of 4HC and 3HC at various pH solutions in the pH range of 2.3–13.4.

There are three isosbestic points for 4HC at 315, 275 and 246 nm and two points for the 3HC at 266 nm and 311 nm. There are two ground state forms of 4HC, one is dominant in acidic solutions and one in basic solutions. Both spectra have a very large overlap. The pK_a value is at about ~ 7.5 . We assign the basic form of 4HC as the deprotonated ORO^- (A) form and the acidic form to the neutral $OROH$ (N) form. The $OROH$ form shows three sub-bands with band peaks at 270, 280 and 304 nm. These sub-bands are assigned to vibrations with $\Delta n \sim 2800$ cm^{-1} and ~ 1350 cm^{-1} . The basic deprotonated form (A) also shows a sub-band structure with



Scheme 1. molecular structure of a. 4-hydroxycoumarin, b. 3-hydroxycoumarin and c. 7-hydroxycoumarin, including coumarin nomenclature.

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