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ARTICLES

Photoinduced Coupled Proton and Electron Transfers. 2. 7-Hydroxyquinolinium Ion

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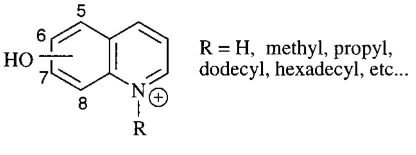
The hydroxyl group of 7-hydroxyquinoline in acidic media (i.e., of 7-hydroxyquinolinium cation, 7-HQ(C)) undergoes photoinduced deprotonation even in strongly acidic media. It occurs from dilute perchloric acid solutions up to 8 mol L^{-1} concentration, which is evidence of an outstanding photoacidity. Excited-state proton ejection was shown to be reversible at acid concentrations greater than 1 mol L^{-1}. Below this value, the proton ejection was not balanced by the proton recombination. Concerning the rates of the excited-state reactions, (i) the proton ejection rate constants k_1 increased upon acid dilution, attaining at high dilution the limiting value of $(k_1)_0 = 5.5 \times 10^{10}$ s^{-1}. k_1 was shown to vary with the water activity according to $k_1 = (k_1)_0(a_{H_2O})^4$. The number 4 is then a key number for the ability of water to accept a proton from 7-HQ(C*). (ii) The proton recombination rate constant varies from 3×10^9 to 4×10^{10} s^{-1} when the acid concentration ranges from 1 to 5 mol L^{-1}. This observation can tentatively be ascribed to a nondiffusional recombination process occurring with the ejected proton in concentrated acid solutions. The results as a whole are consistent with the coupling of an intramolecular electron transfer with the proton transfer, due to the withdrawing effect of the quinolinium function $\geq NH^+$ on the $-O^-$ group generated by the deprotonation. The photoproduct is then most likely to be the ketonic tautomeric form of 7-hydroxyquinoline rather than a zwitterion. Thus, the excited-state behavior is fully accounted for by the photoinduced synergy of the two functional groups.

Introduction

The 5-, 6-, 7-, and 8-hydroxyquinolinium ions (Chart 1) have been mainly used as polarity or pH sensitive probes. The ground-state p*K* of the hydroxyl group is close to the pH of “neutral” aqueous media,[1−4] allowing prototropic equilibria in the range of biological pH (see, for example, the p*K* values of the 1-methylhydroxyquinolinium ions in Table 1).

CHART 1



Moreover, the ground-state deprotonated forms (generally called “oxyquinolinium” because they are thought to be zwit-

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TABLE 1: Ground-State p*K* Values of the Hydroxyl Group of 1-Methyl-5-, 1-Methyl-6-, 1-Methyl-7-, and 1-Methyl-8-hydroxyquinolinium Ions (Room Temperature)

	p*K*	ref
1-methyl-5-hydroxyquinolinum	6.1−6.2	1, 2
1-methyl-6-hydroxyquinolinum	7.0−7.2	1−3
1-methyl-7-hydroxyquinolinum	5.56−5.9	1, 2, 4
1-methyl-8-hydroxyquinolinum	6.8−7.0	1, 2

terionic) show negative solvatochromic shifts in accordance with an intramolecular charge transfer on excitation, decreasing the charge separation. These phenomena are well documented in the case of 1-methyl-6-oxyquinolinium ion,[3] 1-hexacecyl-5-oxyquinolinium, 1-propyl- and 1-hexadecyl-6-oxyquinolinium, and 1-methyl-8-oxyquinolinium ions.[5−10]

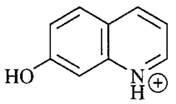
Unfortunately, the 5-, 6-, and 8-oxyquinolinium ions exhibit a very weak fluorescence and can thus only be used as absorption probes. In contrast, the 7-oxyquinolinium ions are fluorescent, whatever the alkyl substituent R (for example, the fluorescence quantum yield of the 1-methyl-7-oxyquinolinium ion is 0.2 in 0.1 mol L^{-1} sodium hydroxyde[11]). For that reason applications based on the fluorescence of these compounds have been proposed. For instance, monitoring the fluorescence intensity of the 1-methyl-7-oxyquinolinium form was used to study the advancement of enzymatic reactions (acetylcholinesterase-catalyzed hydrolysis of either 1-methylacetoxyquinolinium iodides[2,12] or 1-methyl-(7-dimethylcarbamoxy)quinolinium iodide[13]). Another example is the use of the 1-dodecyl derivative as a dye in fluorescence microscopy of giant vesicles.[14]

Concerning the excited-state behavior of the hydroxy forms of the 5-, 6-, 7-, and 8-hydroxyquinolinium ions, it is governed by their strong photoacidities partly due to the well-known enhancement of the −OH group acidity upon excitation in hydroxyaromatic compounds.[15] Consequently, they convert to their deprotonated forms as soon as they are excited in aqueous solutions in the pH range 0−14. This photoacidity of the −OH moiety was first reported from 1959 to 1978[11,16−22] for the N-protonated forms of the hydroxyquinolines (i.e., R = H). The photoinduced proton ejection was further investigated by one of us in 1994 by combining time-resolved measurements with spectral studies in the case of 6-hydroxyquinoline.[3] The 6-hydroxyquinolium ion exhibits such a strong photoacidity that photoinduced deprotonation of the hydroxyl group can occur even in a 10 mol L^{-1} perchloric acid solution! We could establish that this strong photoacidity is due to an intramolecular electron transfer (or charge transfer) coupled to the proton ejection from the −OH group. The presence of the electron-withdrawing moiety $\geq NH^+$ actually amplifies the photoacidity of the −OH group. The intramolecular charge transfer was shown to be the same phenomenon as that observed upon excitation of the oxyquinolinium form and responsible for the abovementionned negative solvatochromic behavior. Unfortunately, the very low fluorescence of the excited-state deprotonated form of the 6-hydroxyquinolinium ion did not allow us to measure its time-dependent rise and decay simultaneously with the decay of the excited hydroxyquinolinium form. The kinetic analysis of the phenomena could then only depend on measurements of the hydroxy form decay.

In this work, use is made of the noticeable fluorescence of both protonated and deprotonated forms of the 7-hydroxyquinolinium ion for studying and refining the understanding of the excited-state processes when the hydroxyl group ejects a proton after excitation. The relationship between the 6- and 7-hydroxyquinolinium will be be confirmed. Moreover, the results presented here will permit us to support the mechanism of tautomerization of 7-hydroxyquinoline in neutral water, whose results will be presented in a forthcoming article.[23]

The 7-hydroxyquinolinium ion under study here is the cationic form of 7-hydroxyquinoline, denoted 7-HQ(C) (Chart 2). Like the 6-hydroxyquinolinium ion, it undergoes photoinduced deprotonation even in concentrated acidic solutions so that the present work is carried out in perchloric acid solutions of various concentrations. The excited-state deprotonated form is a zero net-charge species, a tautomer of the neutral 7-hydroxyquinoline, denoted 7-HQ(T).

CHART 2



7-HQ(C)

Experimental Section

7-Hydroxyquinoline was purchased from Kodak and twice recrystallized from hexane−ethyl acetate. Redistilled perchloric acid from Aldrich containing 69.5% $HClO_4$ (purity: 99.999%) was used to prepare the acidic solutions. These solutions were obtained by weighing appropriate amounts of the concentrated $HClO_4$ solutions in volumetric flasks and by addition of water up to the desired volumes. Thus, the error in the concentration $[HClO_4]$ is less than 0.5%. Millipore filtered water (conductivity of $<1 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ at 25 °C) was employed to prepare the solutions. Anhydrous sodium perchlorate (purity 99%) was supplied by Alfa and used as received.

The measurements in perchloric acidic solutions were done at $HClO_4$ concentrations larger than 10^{-2} mol L^{-1}. Consequently, the ground-state species is always the 7-hydroxyquinolinium ion (7-HQ(C)) because the p*K* of the heterocyclic nitrogen atom of 7-hydroxyquinoline is 5.48.[1]

UV−visible absorption spectra were recorded on a Kontron Uvikon-940 spectrophotometer. The corrected fluorescence spectra were obtained with an SLM 8000C spectrofluorometer.

Most of the decay times were obtained by the single-photon timing technique with picosecond laser excitation. The setup consisted of a mode-locked Coherent Innova 400-10 argon ion laser that synchronously pumped a cavity-dumped Coherent 701-2 dye (rhodamine 6G) laser, delivering 3−4 ps pulses (with ca. 40 nJ/pulse) at a frequency of 3.4 MHz. The laser excitation pulse (λ_{exc} = 300 nm) was recorded slightly away from excitation wavelength with a scattering suspension. Fluorescence was detected through a Jobin-Yvon HR320 monochromator with a grating of 100 lines/mm. The detector employed was a Hamamatsu 2809U-01 microchannel plate photomultiplier. The instrument response function had an effective fwhm of 35 ps.

The measurements of the decay times of 7-HQ(C*) in 11.7, 10.7, and 8.88 mol L^{-1} $HClO_4$ and of 7HQ(T*) in water (single exponential decays) were carried out with a multifrequency phase-modulation fluorometer equipped with a Pockels cell operating at frequencies from 10 to 190 MHz. The excitation sources were two He−Cd lasers at either λ_{exc} = 325 nm for 7-HQ(C*) in acidic solutions or λ_{exc} = 442 nm for 7-HQ(T*) in water.

For the time-resolved experiments the concentration of the solutions in 7-HQ was 1.5×10^{-5} mol L^{-1}. The temperature of the samples was 25 °C (thermostated compartment). The data were analyzed by a nonlinear least-squares method using Globals

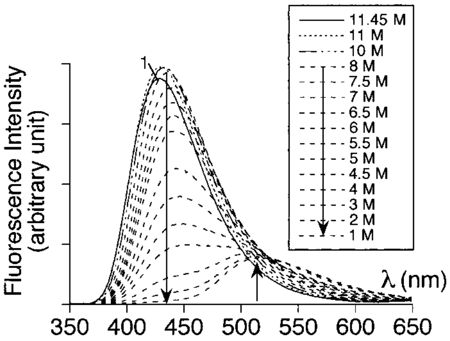


Figure 1. Corrected emission spectra of 7-HQ(C*) in aqueous perchloric solutions ($\lambda_{\mathrm{exc}} = 340$ nm). Spectrum 1 was recorded in 11.45 mol L^{-1} $HClO_4$. The other spectra were recorded in progressively more diluted solutions.

software (Globals Unlimited, University of Illinois at Urbana—Champaign, Laboratory for Fluorescence Dynamics).

Results

The absorption spectra of the 7-hydroxyquinolinium ion (1.5×10^{-5} mol L^{-1}) were recorded in perchloric acid solutions progressively diluted from 11.45 to 0.1 mol L^{-1}. The shape and the height of the absorption band of the ground-state cationic 7-HQ(C) species were not noticeably modified by dilution. Only a slight red shift was observed; the absorption maximum wavelength was shifted from 346 to 348 nm when the acid concentration decreased from 11.45 to 7 mol L^{-1}. Upon further dilution the additional bathochromic shift did not exceed 1 nm, the absorption maximum wavelength being 349 nm in 0.1 mol L^{-1} $HClO_4$.

The fluorescence emission spectra were recorded in the same $HClO_4$ concentration range (Figure 1). For the largest acid concentrations (11.45−10 mol L^{-1}), the spectrum consisted of an emission band of the excited protonated form 7-HQ(C*), whose maximum was shifted from 428 to 433 nm on dilution. The increase of the emission intensity when going from 11.45 to 10 mol L^{-1} can be accounted for by the weakening of quenching due to the perchloric acid. Further dilution to and below 8 mol L^{-1} led to a marked decrease of the 7-HQ(C*) band concomitantly with an additional red shift ($\lambda_{\max} = 441-442$ nm for $[HClO_4] = 6-5$ mol L^{-1}) and a broadening of the band at wavelengths larger than 500 nm. This decrease can be interpreted as a result of the excited-state deprotonation reaction, in a similar way as for the 6-hydroxyquinolinium ion.[3] Below $[HClO_4] = 6.5$ mol L^{-1}, the broadening of the 7-HQ(C*) band is clearly due to the growth of the band of the deprotonated species, 7-HQ(T*), whose maximum is around 516 nm, as observed in 1 or 0.1 mol L^{-1} $HClO_4$ solutions.

The time-resolved measurements were carried out after excitation of 7-HQ(C) in acidic solutions whose concentrations ranged from $[HClO_4] = 11.7$ to 10^{-2} mol L^{-1}. The ionic strength was only due to the presence of perchloric acid except for one experiment carried out with a sodium perchlorate concentration of 4 mol L^{-1} in the presence of 10^{-2} mol L^{-1} perchloric acid. The decays were monitored at 420 and at 550 nm, and the time constants given in Table 2 were calculated from the following observations.

(i) For $[HClO_4] \geq 8.88$ mol L^{-1}, a single-exponential fluorescence decay was observed whatever the observation wavelength. A slight increase in the decay times was observed when going from $[HClO_4] = 11.7$ to 8.88 mol L^{-1} consistently with the increase of the fluorescence intensity. (ii) For 1.02 mol L^{-1} $\leq [HClO_4] \leq 8.00$ mol L^{-1}, the decays recorded at 420 and 550 nm were biexponential, and the corresponding decay times could be determined with a fairly good accuracy. The rise time τ_1 observed at 550 nm corresponded to the decay time τ_1 observed at 420 nm, and the decay time τ_2 observed at 550 nm corresponded to the decay time τ_2 observed at 420 nm except for $[HClO_4] = 1.02$ mol L^{-1}, where the intensity of the fluorescence emission at 420 nm (see Figure 1) was very weak, not allowing an accurate measurement. (iii) For $[HClO_4] \leq 0.1$ mol L^{-1}, only the biexponential fluorescence decay at 550 nm could be recorded except for the measurement carried out in the presence of sodium perchlorate ($[HClO_4] = 10^{-2}$ mol L^{-1} and $[NaClO_4] = 4$ mol L^{-1}). The presence of $NaClO_4$ allowed a measurable signal to be observed at 420 nm, which could be analyzed as a single-exponential decay ($\tau_1 = 61$ ps). At 550 nm, the decay time τ_2 was independent of the acid concentration and of the addition of $NaClO_4$ ($\tau_2 = 2.67 \pm 0.01$ ns). This decay time was shown to be the lifetime τ_T of the tautomer 7-HQ-(T*), which was independently determined by direct excitation at 442 nm of the ground-state 7-HQ(T) form in a neutral aqueous solution.

TABLE 2: Decay Times Determined at 420 and 550 nm in Perchloric Acid Solutions of 7-HQ(C)

$[HClO_4]^a$ mol L^{-1}	420 nm τ_1 (ps) decay	420 nm τ_2 (ns) decay	550 nm τ_1 (ps) rise	550 nm τ_2 (ns) decay
11.70	*b*	$9.7_1 \pm 0.1$		
10.70	*b*	$9.8_2 \pm 0.1$		
10.00	*b*	9.9 ± 0.1		
8.88	*b*	$10.0_5 \pm 0.1$		
8.00	*d*	10.0 ± 0.1	77 ± 5	$9.9_5 \pm 0.1$
7.00	35 ± 5	9.5 ± 0.1	50 ± 5	9.5 ± 0.1
6.00	31 ± 5	8.5 ± 0.15	31 ± 5	$8.5_1 \pm 0.1$
5.02	18 ± 5	6.70 ± 0.05	22 ± 5	6.81 ± 0.05
4.00	26 ± 5	5.10 ± 0.05	20 ± 5	5.01 ± 0.05
3.02	22 ± 5	3.70 ± 0.05	23 ± 5	3.77 ± 0.05
2.06	20 ± 5	3.14 ± 0.05	21 ± 5	3.14 ± 0.05
1.02	*c*	*c*	21 ± 5	2.81 ± 0.05
0.10	*c*	*c*	19 ± 5	2.68 ± 0.05
0.01	*c*	*c*	18 ± 5	2.67 ± 0.05
0.01 (and $[NaClO_4]$ = 4 mol L^{-1})	61 ± 5	*b*	60 ± 5	2.67 ± 0.05

[a] The error in the concentration of $HClO_4$ is estimated to be less than 0.5% (see Experimental Section). [b] Single-exponential decay. [c] The decay times could not be determined with enough accuracy because of the low level of light. [d] Not measured.

Discussion

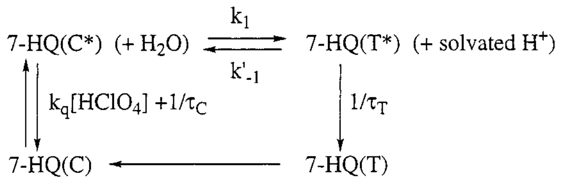
The rate constants of the excited-state processes can be calculated in each of the three above-mentioned ranges of perchloric acid concentration.

(i) For $[HClO_4] \geq 8.88$ mol L^{-1}, the only emitting species is 7-HQ(C*). The red shifts in the absorption and fluorescence spectra observed by dilution of the 11.45 mol L^{-1} perchloric acid may be due to the decrease of the ionic strength when the concentrated perchloric acid is diluted. A similar effect was observed with the 6-hydroxyquinolinium ion.[3] The increase in the fluorescence intensity and in the decay time τ_2 observed upon dilution of the most concentrated acid solution is consistent with the existence of a quenching effect due to $HClO_4$. The experimental values of the decay rate constant $1/\tau_2$ calculated as a function of the perchloric acid concentration were found to follow the Stern−Volmer relation:

$$\frac{1}{\tau_2} = \frac{1}{\tau_C} + k_q[HClO_4]$$

where τ_C is the lifetime of the 7-HQ(C*) form and k_q the quenching rate constant. The regression coefficient was 0.999 11, $\tau_C = 11.3$ ns, and $k_q = 1.2_3 \times 10^6$ mol^{-1} L s^{-1}. The quite low value of k_q shows that the characteristic times of the quenching phenomenon are long compared to the lifetime of 7-HQ(C*) and compared to the duration of the photoinduced deprotonation reaction (see below).

SCHEME 1



(ii) For 1.02 mol L^{-1} ≤ [HClO$_4$] ≤ 8.00 mol L^{-1}, the excited-state deprotonation occurs with an efficiency that increases upon dilution. As shown in the fluorescence spectra, the emission at 420 nm arises from 7-HQ(C*). At 550 nm the emissions of 7-HQ(C*) and 7-HQ(T*) are superimposed. The time-resolved data (Table 2) were interpreted according to the conventional scheme of an excited-state process (Scheme 1). k_1 is the proton ejection rate constant and k_{-1}' the pseudo-first-order rate constant for proton recombination. The quenching of fluorescence of the deprotonated form 7-HQ(T*) form by HClO$_4$ is likely to be negligible because of the observation of an isoemissive point on the emission spectra at 522 nm when [HClO$_4$] ≤ 7.00 mol L^{-1} (Figure 1). The rate equations are

$$\frac{d[C^*]}{dt} = -\left\{\frac{1}{\tau_C} + k_q[HClO_4] + k_1\right\}[C^*] + k_{-1}'[T^*]$$

$$\frac{d[T^*]}{dt} = k_1[C^*] - \left\{\frac{1}{\tau_T} + k_{-1}'\right\}[T^*]$$

Thus, a biexponential decay for both 7-HQ(C*) and 7-HQ(T*) is expected:

$$[C^*] = \frac{[C^*]_0}{\beta_2 - \beta_1}[(\beta_2 - \alpha)\, e^{-t/\tau_1} + (\alpha - \beta_1)\, e^{-t/\tau_2}]$$

$$[T^*] = \frac{[C^*]_0 k_1}{\beta_2 - \beta_1}[e^{-t/\tau_1} - e^{-t/\tau_2}]$$

where

$$\alpha = 1/\tau_C + k_q[HClO_4] + k_1$$

$$\tau_1 = 1/\beta_1 \qquad \tau_2 = 1/\beta_2$$

β_1 and β_2 are solutions of $\beta^2 - S\beta + P = 0$ with

$$S = \beta_1 + \beta_2 = 1/\tau_C + 1/\tau_T + k_1 + k_q[HClO_4] + k_{-1}'$$

$$P = \beta_1\beta_2 = \frac{1}{\tau_C\tau_T}[1 + (k_1 + k_q[HClO_4])\tau_C + k_{-1}'\tau_T]$$

The rate constants k_1 and k_{-1}' were calculated from the sum $S = \beta_1 + \beta_2$, the product $P = \beta_1\beta_2$, and the k_q value (1.23×10^6 mol^{-1} L s^{-1}); however, the low contribution of the quenching process (k_q[HClO$_4$] = 9.8×10^6 s^{-1} for [HClO$_4$] = 8.00 mol L^{-1} and 1.25×10^6 s^{-1} for [HClO$_4$] = 1.02 mol L^{-1}) must be remembered. The results are given in Table 3.

TABLE 3: Rate Constants for Deprotonation (k_1) and Proton Recombination (k_{-1}') of 7-HQ(C*) in HClO$_4$ Solutions

[HClO$_4$]^a mol L^{-1}	k_1^{b} s^{-1}	k_{-1}' ^{b} s^{-1}	a_{H_2O}^{c}
8.00	$7.8_3 \times 10^7$	$1.2_5 \times 10^{10}$	0.1937
7.00	$6.3_3 \times 10^8$	$2.2_5 \times 10^{10}$	0.3182
6.00	$2.5_7 \times 10^9$	$3.0_4 \times 10^{10}$	0.4607
5.02	$9.5_1 \times 10^9$	$4.0_1 \times 10^{10}$	0.6001
4.00	$1.6_1 \times 10^{10}$	2.7×10^{10}	0.7282
3.02	$2.6_5 \times 10^{10}$	$1.6_6 \times 10^{10}$	0.8283
2.06	$3.8_1 \times 10^{10}$	$9.3_4 \times 10^9$	0.9026
1.02	$4.4_4 \times 10^{10}$	3.1×10^9	0.9601
0.10	$5.2_5 \times 10^{10}$	*d*	0.9966
0.01	$5.5_4 \times 10^{10}$	*d*	1.0000
0.01 (and [NaClO$_4$] = 4 mol L^{-1})	$1.6_4 \times 10^{10}$	*d*	

[a] The error in the concentration of HClO$_4$ is estimated to be less than 0.5% (see Experimental Section). [b] The error in the rate constants is smaller than 25% for the acid concentrations of 6, 7, and 8 mol L^{-1} and less than 15% for the acid concentrations lower than 6 mol L^{-1}. [c] Activity of water calculated from osmotic coefficients in HClO$_4$ solutions.[30] [d] No back-proton recombination is observed.

(iii) For [HClO$_4$] ≤ 0.1 mol L^{-1}, the decay time τ_2 of the 7-HQ(T*) form was found to be equal to its lifetime ($\tau_2 = \tau_T = 2.67 \pm 0.01$ ns). This means that the proton recombination is much slower than both proton ejection and deexcitation of 7-HQ(C*). Under these conditions, proton ejection is irreversible and the previous equations become

$$\frac{d[C^*]}{dt} = -\left\{\frac{1}{\tau_C} + k_1 + k_q[HClO_4]\right\}[C^*]$$

$$\frac{d[T^*]}{dt} = k_1[C^*] - \frac{1}{\tau_T}[T^*]$$

which lead to

$$[C^*] = [C^*]_0\, e^{-t/\tau_1}$$

$$[T^*] = \frac{[C^*]_0 k_1}{k_1 + k_q[HClO_4] + \dfrac{1}{\tau_C} - \dfrac{1}{\tau_T}}[e^{-1/\tau_T} - e^{-t/\tau_1}]$$

where

$$\tau_1 = \left[\frac{1}{\tau_C} + k_q[HClO_4] + k_1\right]^{-1}$$

The equations also show that the 7-HQ(C*) decay must be a single exponential. The only experiment allowing us to record the decay of C* at 420 nm was, in the relevant pH range, the experiment in the presence of NaClO$_4$ (see above). In fact the 7-HQ(C*) experimental decay was single exponential with a time constant similar to the rise time of the 7-HQ(T*) form, in accordance with the above equations.

The rate constants were calculated, and Table 3 was completed. The rate constants values now have to be discussed and understood as a whole.

The proton ejection rate constant from 7-HQ(C*) at infinite dilution $(k_1)_0$ is basically the same as the rate constant determined in $[HClO_4] = 0.01$ mol L^{-1}, i.e., $(5.5 \pm 0.6) \times 10^{10}$ s^{-1}. This value is larger than the corresponding rate constants for compounds that are well-known for their character of strong acids in the excited state, such as pyranine (8.0×10^9 to 1.5×10^{10} s^{-1})[24,25] and 1-naphthol (2.5×10^{10} s^{-1}).[26] But 7-HQ(C*) should rather be compared to photoacids bearing an electron-withdrawing substituent such as the cyano-2-naphthols synthesized by Tolbert;[27] $(k_1)_0$ for 7-HQ(C*) is also larger than the deprotonation rate constants of the 6-, 7-, and 8-cyano-2-naphthols in water and close to that of 5-cyano-2-naphthols (7×10^{10} s^{-1}, the error given by the authors in the determination of this value being ~20%).[28] The remarkable tendency of 7-HQ(C*) to undergo photoinduced proton dissociation is thus brought to the fore.

Let us now compare the 6- and 7-hydroxyquinolinium ions. The spectral data showed that deprotonation was already efficient in 10 mol L^{-1} perchloric acid for 6-HQ(C*) (see Introduction), while it only began in 8 mol L^{-1} perchloric acid for 7-HQ(C*). An outstanding proton ejection constant for 6-HQ(C*), larger than 5.5×10^{10} s^{-1}, can then be expected. However, the rate constant given by us in ref 3 for 6-HQ(C*) is 1 order of magnitude lower. In fact, in the measurements done by us at that time, only the emission of the C* form was analyzed because of the extremely weak fluorescence of the T* form (see Introduction). It might then be possible that a very short second component was missed in the strong C* emission (lifetime: 25 ns) because the phase-modulation fluorometry technique used in this first study was less accurate (in the case of multiexponential decays of very different time constants) than the single-photon timing technique. For this reason, the rate constants values determined in the previous work on the 6-hydroxyquinolinium ion[3] are unfortunately not to be compared to that obtained here for the 7-hydroxyquinolinium ion.

Table 3 shows that the proton ejection rate constant decreases when the acid concentration increases. This may be due to an ionic strength effect because the rate constant determined in 0.01 mol L^{-1} perchloric acid alone, supposed to be the rate constant at infinite dilution $(k_1)_0$, decreases when 4 mol L^{-1} $NaClO_4$ is added and becomes equal to the rate constant in 4 mol L^{-1} $HClO_4$ ($k_1 = 1.6 \times 10^{10}$ s^{-1}).

The data for k_1 were then analyzed according to the following empirical expression:[24,29]

$$k_1 = (k_1)_0(a_{H_2O})^n$$

where a_{H_2O} is the activity of water and n an empirical parameter roughly associated with the number of water molecules involved in the proton-transfer step. The activity of water was calculated from osmotic coefficients in $HClO_4$ solutions.[30] The experimental results fit well the linear function

$$\ln k_1 = \ln(k_1)_0 + n \ln(a_{H_2O})$$

with $n = 3.96$ (regression coefficient: 0.999 12) (Figure 2). Such a result can revive the controversy about the requirement of clusters of four water molecules as proton acceptors in water.[31-35] However, hydration ring-structures with four water molecules were recently shown to occur in concentrated HCl solutions and proposed to represent short-lived intermediates along the acid dissociation path, even in less concentrated solutions.[36]

Concerning the back-recombination process, two features must be emphasized: (i) No proton recombination was observed below $[HClO_4] = 1.02$ mol L^{-1}; (ii) the pseudo-first-order rate constants reported in Table 3 for $[HClO_4] \geq 1.02$ mol L^{-1} were slightly modified by the variation of the perchloric acid concentration.

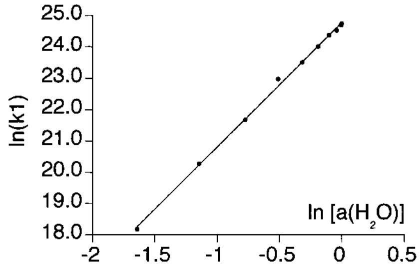


Figure 2. Linear fit of the logarithm of the proton ejection rate constant as a function of the logarithm of the water activity.

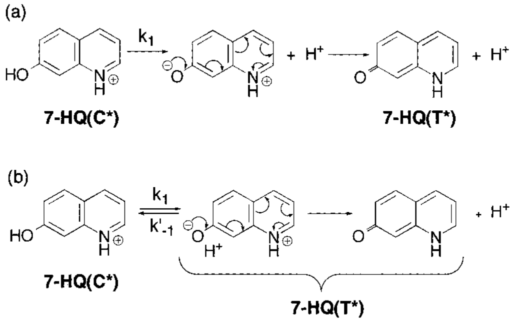


Figure 3. Scheme of the excited-state processes in 7-HQ(C*): (a) in $[HClO_4] < 1$ mol L^{-1} solutions; (b) in $[HClO_4] \geq 1$ mol L^{-1} solutions. k_1 is the proton ejection rate constant. k_{-1}' is the pseudo-first-order rate constant for proton recombination.

The absence of proton recombination at perchloric acid concentrations of 0.1 and 0.01 mol L^{-1} seems surprising if a diffusional process took place. The rate constant of a diffusional protonation reaction in dilute aqueous solutions is about 5×10^{10} mol^{-1} L s^{-1}.[37] Thus, a reprotonation in 0.1 and 0.01 mol L^{-1} $HClO_4$ should occur in less than 1 ns and consequently be observed during the overall excited-state process. The explanation of this phenomenon has already been thoroughly argued in the case of 6-hydroxyquinolinium ion;[3] an intramolecular electron transfer is coupled with the proton ejection, draining off the negative charge from the deprotonation site $-O^-$ and impairing back-recombination. The structure of the photoproduct 7-HQ(T*) is then ketonic as shown in Figure 3a.

In concentrated acidic solutions, i.e., for $[HClO_4] \geq 1.02$ mol L^{-1}, a back-recombination is observed whose rate is not consistent with a diffusional process because it does not monotonically increase with the acid concentration. An explanation of this could be that at large acid concentrations part of the ejected protons remains close to the oxy group $-O^-$, impairing the intramolecular charge transfer and allowing recombination to occur. The deprotonated form 7-HQ(T*) could then be shared between zwitterionic species where the ejected proton remains ion-paired to the hydroxylate moiety and ketonic structures as those proposed above. Proton recombination would then occur within the intermediate ion pairs (Figure 3b). This phenomenon would be due to the acidity of the medium rather than to an ionic strength or viscosity effect because no back-recombination was observed in 4 mol L^{-1} $NaClO_4$.

Conclusion

The excited-state deprotonation of the hydroxyl group of the bifunctional 7-hydroxyquinolinium ion is observed even in acid medium and is effective up to 8 mol L^{-1} $HClO_4$. The efficiency of the phenomenon is of course improved by the dilution of the acid. Both proton ejection and proton recombination rates were determined and discussed.

The increase of the proton ejection rate constant when the acid is diluted can be ascribed to the lowering of the ionic strength. The analysis of the results shows that “4” is a key number regarding the number of water molecules accepting the proton.

In concentrated acidic media (1.02 mol $L^{-1} \leq [HClO_4] \leq$ 8.00 mol L^{-1}), proton back-recombination is observed and occurs at rates that do not seem to be significantly dependent on the acid concentration. This observation is consistent with some ion-pairing, competing with the proton escape. The observed proton back-recombination could be the reprotonation of the oxyquinolinium ions within ion pairs.

At large dilutions, the rate of the phoinduced proton ejection attains its limiting value $(k_1)_0 = (5.5 \pm 0.6) \times 10^{10}\ s^{-1}$. This great value is accounted for by the presence of the electron-withdrawing $\geq NH^+$ on the neighboring ring, which drives the negative charge of the hydroxylate $-O^-$ away, impairing its back-reprotonation and leading to a ketonic structure of the deprotonated form 7-HQ(T*). An intramolecular electron transfer is then coupled with the proton transfer, and the phenomena must be understood considering the photoinduced synergy between the two functional groups.

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References and Notes

(1) Mason, S. F. *J. Chem. Soc.* **1958**, 674.

(2) Prince, A. K. *Arch. Biochem. Biophys.* **1966**, *113*, 195.

(3) Bardez, E.; Chatelain, A.; Larrey, B.; Valeur, B. *J. Phys. Chem.* **1994**, *98*, 2357.

(4) Epstein, D. J.; Berman, H. A.; Taylor, P. *Biochemistry* **1979**, *18*, 4749.

(5) Drummond, C. J.; Grieser, F.; Healy, T. W. *J. Phys. Chem.* **1988**, *92*, 2604.

(6) Kumoi, S.; Oyama, K.; Yano, T.; Kobayashi, H.; Ueno, K. *Talanta* **1970**, *17*, 319.

(7) Drummond, C. J.; Grieser, F.; Albers, S. *Colloid Surf.* **1991**, *54*, 197.

(8) Philips, J. P.; Keown, R. W. *J. Am. Chem. Soc.* **1951**, *73*, 5483.

(9) Saxena, J. P.; Stafford, W. H.; Stafford, W. L. *J. Chem. Soc.* **1959**, 1579.

(10) Ueda, M.; Schelly, Z. A. *Langmuir* **1989**, *5*, 1005.

(11) Mason, S. F.; Philip, J.; Smith, B. E. *J. Chem. Soc. A* **1968**, 3051.

(12) Prince, A. K. *Biochem. Pharmacol.* **1966**, *15*, 411.

(13) Rosenberry, T. L.; Bernhardt, S. A. *Biochemistry* **1971**, *10*, 4114.

(14) Menger, F. M. *Langmuir* **1996**, *12*, 4479.

(15) (a) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131. (b) Arnaut, L. G.; Formosinho, S. J. *J. Photochem. Photobiol. A* **1993**, *75*, 1 and references therein.

(16) Popovych, O.; Rogers, L. B. *Spectrochim. Acta* **1959**, *15*, 584.

(17) Goldman, M.; Wehry, E. L. *Anal. Chem.* **1970**, *42*, 1178.

(18) Ballard, R. E.; Edwards, J. W. *J. Chem. Soc.* **1964**, 4868.

(19) Schulman, S.; Fernando, Q. *Tetrahedron* **1968**, *24*, 1777.

(20) Bratzel, M. P.; Aaron, J. J.; Winefordner, J. D.; Schulman, S. G.; Gershon, H. *Anal. Chem.* **1972**, *44*, 1240.

(21) Sawada, T.; Kamada, H. *Bunseki Kagaku* **1976**, *25*, 243.

(22) Onoue, Y.; Hiraki, K.; Morishige, K.; Nishikawa, Y. *Nippon Kagaku Kaishi* **1978**, *9*, 1237.

(23) Bardez, E.; Fedorov, A.; Berberan-Santos, M. N.; Martinho, J. M. G.; Larrey, B. To be published.

(24) Bardez, E.; Goguillon, B. T.; Keh, E.; Valeur, B. *J. Phys. Chem.* **1984**, *88*, 1909.

(25) Pines, E.; Huppert, D.*Chem. Phys. Lett.* **1986**, *126*, 88.

(26) Krishnan, R.; Lee, J.; Robinson, G. W. *J. Phys. Chem.* **1990**, *94*, 6365.

(27) (a) Tolbert, L. M.; Haubrich, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 8163. (b) Tolbert, L. M.; Haubrich, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 10593.

(28) Huppert, D.; Tolbert, L. M.; Linares-Samaniego, S. *J. Phys. Chem. A* **1997**, *101*, 4602.

(29) Huppert, D.; Kolodney, E.; Gutman, M.; Nachliel, E. *J. Am. Chem. Soc.* **1982**, *104*, 6949.

(30) (a) Hamer, W. J.; Wu, Y. C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1062. (b) Wai, H.; Yates, K. *Can. J. Chem.* **1969**, *47*, 2326.

(31) Lee, J.; Griffin, R. D.; Robinson, G. W. *J. Chem. Phys.* **1985**, *82*, 4920.

(32) Lee, J.; Robinson, G. W.; Webb, S. P.; Philips, L. A.; Clark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 6538.

(33) Krishnan, R.; Fillingim, T. G.; Lee, J.; Robinson, G. W. *J. Am. Chem. Soc.* **1990**, *112*, 1353.

(34) Yao, G. H.; Lee, J.; Robinson, G. W. *J. Am. Chem. Soc.* **1990**, *112*, 5698.

(35) Shizuka, H.; Ogiwara, T.; Narita, A.; Sumitani, M.; Yoshihara, K. *J. Phys. Chem.* **1986**, *90*, 6708.

(36) Agmon, N. *J. Phys. Chem. A* **1998**, *102*, 192.

(37) Gutman, M.; Nachliel, E. *Biochem. Biophys. Acta* **1990**, *1015*, 391.