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 23. Compound **14**: ^1H NMR (300 MHz, CDCl_3) δ 0.86 (d, $J=6.6$ Hz, 6H), 1.12-1.80 (m, 17H), 1.48 (s, 9H), 2.28-2.48 (m, 2H), 3.09 (brs, 1H), 3.96 (m, 1H). Acetylated

t-butylester was also obtained as a side product but readily converted to compound **14** by hydrolysis with aqueous 1 M KOH.

24. Compound **15**: $[\alpha]_D^{24} +1.13^\circ$ (c 0.8, CHCl_3); IR (neat) 1157, 1368, 1746, 2853, 2922, 2971 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.86 (d, $J=6.6$ Hz, 6H), 1.01 (d, $J=6.5$ Hz, 3H), 1.10-1.64 (m, 18H), 1.43 (s, 9H), 2.16-2.55 (m, 6H), 3.67 (s, 3H), 5.22 (m, 1H); MS (Cl., CH_4) m/z (%) 443 (M^+ , 2), 387 (100), 370 (2), 355 (9), 255 (2), 227 (7), 161 (7), 143 (27).

Observation of Both Electron and Proton Transfers in the Lowest Triplet as Well as Ground State Potential of Aqueous 6-Hydroxyquinoline

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The transfer reaction of charge as electron or proton is one of the most attractive fields of chemical study since it is not only omnipresent but also very important in a variety of chemical and biological processes. Photoinduced proton and electron transfer reactions in numerous molecular systems have been extensively studied recently using various time-resolved laser spectroscopic techniques.¹⁻⁷ The investigations not only provide us the vivid pictures of the reaction processes but also facilitate understanding the relations of various different properties to one another systematically. In some cases electron⁸⁻¹⁰ and proton^{1,11} transfers occur in the lowest triplet states as well. Nevertheless, very few cases have been reported in which both electron and proton transfer reactions are directly involved in the lowest triplet state potential. Even in these cases the transfers were asserted to take part in complicated photochemical processes involving exciplex formation.¹² In this brief report we show that both electron and proton reverse transfer reactions take place not only in the ground states of aqueous 6-hydroxyquinoline (6HQN) equilibrium species but also in their lowest triplet states and that the simple molecular system of 6HQN suits a good model system with which we can study consecutive proton and electron transfer reactions in a single triplet potential curve systematically.

Hydroxyquinolines and their derivatives show interesting phenomena in both fundamental and practical points of view.¹³⁻¹⁷ The normal molecule (HQN) of aqueous 6HQN in the first excited singlet state, produced by pulse excitation, has been reported³ to undergo protonation to the imine group first in 15 ps to transform into imine-protonated cation (HQN^+), then in the time scale of 40 ps deprotonation from the enol group to turn into imine-protonated and enol-deprotonated zwitterion (QNH^+). Finally, however, quickly as in 11 ps the photochemically produced excited QNH^+ goes through intramolecular electron transfer from

the deprotonated oxygen atom to the positively charged iminium ring to change into a resonance hybrid structure of quinoid-prevailing forms (QNH') as presented in Figure 1.³

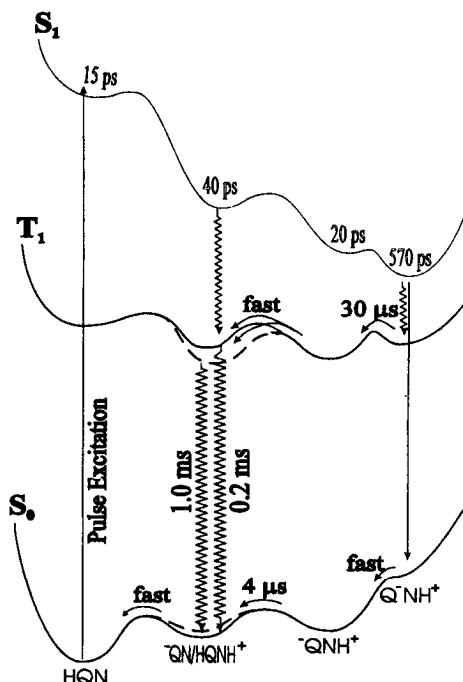


Figure 1. Schematic representation of proton and electron transfers in the first excited singlet, lowest triplet and ground states of aqueous 6HQN equilibrium species at a neutral pH. The relaxation time constants of the respective first excited singlet states are cited from the ref. 3. The relative positions of the electronic states of QN, especially compared with those of HQN^+ drawn with solid lines, are indicated by dotted curves.

The photochemically transformed QNH^+ species in S_1 relaxes with a decay time constant of 570 ps³ into the lowest triplet or ground state. In neutral pH solutions enol-deprotonated anion (QN) was reported³ not to be brought to birth as a reaction intermediate in S_1 potential, although its potential is known¹³ to be relatively lower than that of HQNH⁺ in S_1 .

6HQN and 6-methoxyquinoline (6MQN), purchased from the Aldrich, were vacuum-sublimated and used as received, respectively, and 1-methyl-6-hydroxyquinolinium iodide (6HQNMI), prepared following the procedure described in the ref. 14, was recrystallized, before they were dissolved in distilled water or in NaOH or HCl aqueous solutions to produce appropriate samples. Static absorption and emission spectra were measured using respective home-made spectrometers. Time-resolved transient absorption spectra and kinetic profiles were obtained by monitoring transmittance changes of Xe lamp (Sochoeffel, LPS 255) beam passing through a sample, which was excited by 0.6-ns N₂ laser (Laser Photonics, LN1000) pulses. The probe beam, wavelength-selected using two 0.25-m monochromator (Kratos, GM 252), was detected with a photomultiplier tube (Hamamatsu, R928) and digitized with a 200-MHz oscilloscope (Tektronix, TDS 350) which was interfaced to a 486 PC computer. The laser and the oscilloscope were triggered with variable delays by a pulse/delay generator (SRS, DG 535).

Figure 2 shows time-resolved transient absorption spectra measured after excitation of HQN species. At least three different transient absorption bands can be found: absorption bleach band at 320 nm and transient absorption bands near 370 and 520 nm. However, five different transient absorption bands have been ascertained after careful examinations of transient absorption kinetic profiles as well as time-resolved transient absorption spectra of 6HQN, 6MQN and 6HQNMI aqueous solutions at various pHs. Comparing

two transient spectra measured at the delays of 5 and 50 μ s, we can notice that the transient absorption at 390 nm decays faster than that at 350 nm. Transient absorption at 390 nm decays in 4 μ s in neutral solutions and is assigned to the absorption of transient QNH^+ species in S_0 while the absorption at 350 nm decays in 30 μ s and is designated to the absorption of QNH^+ in T_1 . The transient absorption at 520 nm decays biphasically with the time constants of 0.2 ms (91%) and 1.0 ms (9%) but it also rises biphasically with instant (26%) and 30- μ s (74%) time constants. The fast decaying transient absorption at 520 nm is ascribed to the absorption of HQNH⁺ in T_1 while the slowly decaying one to the absorption of QN in T_1 , although both absorption bands are not distinguishable spectrally with our current spectral resolution. The instantly rising component of 520-nm transient absorption band, in the time scale of microseconds, should originate from the intersystem crossing of HQNH⁺ in S_1 . It should also be noted that the relative amplitude of the instantly rising component is larger than that of the slowly decaying component, supporting that the slowly decaying absorption with 9% relative decay amplitude should be accounted for the absorption of transient QN (rather than HQNH⁺) species in T_1 .

The results of time-resolved transient absorption studies on the reverse electron and proton transfer processes of aqueous 6HQN equilibrium species at near neutral pHs are summarized in Figure 1. It is interesting to note that intramolecular electron transfer is slower in T_1 but faster in S_0 than either protonation to negatively charged oxygen atom or deprotonation from iminium group. We can explain these opposite behaviors in the T_1 and S_0 potentials by considering the differences in the generally known characters of T_1 and S_0 states. The lowest triplet states of both (π,π') and (n,π') are diradicaloid and unconcerned while the ground state of S_0 has more concerted character.¹⁸ In addition, protonation and deprotonation processes are rad-

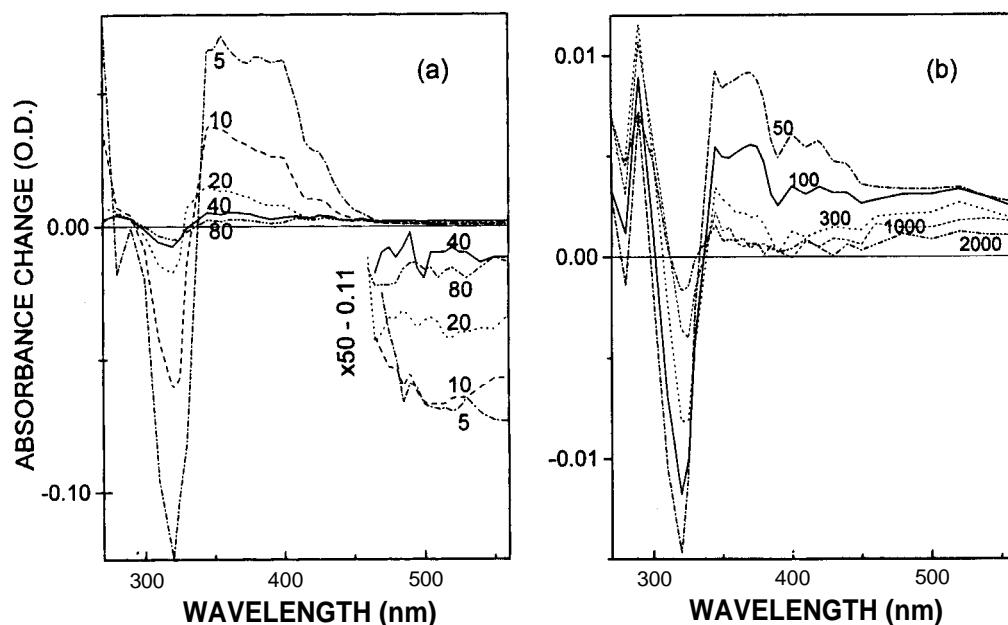


Figure 2. Transient absorption spectra of 6HQN aqueous neutral solution in relatively short (a) and long (b) delay times. The sample was excited at 337 nm and the delay times in microseconds between excitation and measurement are indicated near the respective spectra.

icaloid characteristically so that they do not require concerted characters as badly as intramolecular electron transfer process. If there were no character differences between T_1 and S_0 potentials, electron transfer would be faster than proton transfer in both T_1 and S_0 , admitting that the potential of QNH^+ , compared with that of QN^+ , is expected to be less unstable in T_1 than in S_0 . We attribute the faster relaxation of the lowest triplet state of HQN^+ species, compared with the relaxation of the lowest triplet state of QN species, to the enhanced intersystem crossing rate of the lowest triplet state into the ground state by the vibrations of the O-H and N-H groups that exist exclusively in HQN^+ species. The observation of transient absorption due to ground state QNH^+ species indicates that the very weak fluorescence³ and unobservable ground state absorption of QNH^+ species are attributable to the energetically unfavorable potentials rather than to its unfavorable transition¹⁴ between S_1 and S_0 .

In this short and preliminary report we have tried to reveal that both the reverse electron and proton transfer reactions take place in the lowest triplet state potential of 6HQN as well as in its ground state potential. Further extensive studies, the results of which we will report later, on the consecutive electron and proton transfer reactions in T_1 of simple 6HQN and its derivative molecular systems would shed light on the currently barely understood roles of the lowest triplet state potential in proton and electron transfer processes in general.

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Nucleophilic Addition on Nitrogen : Azophilic Addition of Grignard Reagent to 1-Benzyl Tetrazole Substituted Imine

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Tetrazole have been the primary choice for medicinal chemists as a carboxylic acid isostere because of their similar acidity ($pK_a \approx 5$) to that of the parent carboxylic acid and their stability against metabolism.¹ Recently, particularly in connection with the development of nonpeptidic receptor antagonists of the vasoactive octapeptide angiotensin II, there has been renewed interest in the chemistry of tetrazoles.² In connection with our research programs of designing enzyme inhibitors and receptor antagonists, we needed various tetrazole analogs as amino acid isosteres.³ To this

end, we have examined a synthetic methodology based on a nucleophilic addition of the Grignard reagents on imines and herein we would like to report unexpected findings regarding the regioselectivity in the addition reaction.

There are numerous literature precedents on this type of reactions and it has been known that in most cases the organometallic addition to imines proceeds with a nucleophile attack normally on the carbon atom (carbophilic addition) instead of the nitrogen atom (azophilic addition).⁴ This type of the reaction, particularly, the reaction of organometallic