Laser Flash Photolysis Study on Hydrogen Atom Transfer of 2-(2-Hydroxyphenyl)benzoxazole and 2-(2-Hydroxyphenyl)benzothiazole in the Triplet Excited State

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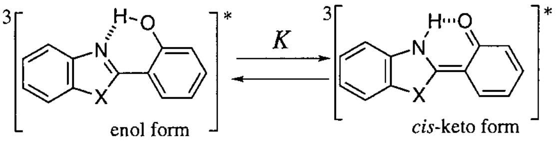
We have revealed that 2-(2-hydroxyphenyl)benzoxazole (HBO) and 2-(2-hydroxyphenyl)benzothiazole (HBT) underwent hydrogen atom transfer in the triplet excited state in benzene at room temperature and the equilibrium constants between the enol form and the *cis*-keto form were estimated.

The excited state intramolecular proton or hydrogen atom transfer (ESIPT) reaction of HBO and HBT has been extensively studied from the view point of reaction dynamics.[1] On direct irradiation the enol form of HBO and HBT underwent excited state intramolecular hydrogen atom transfer to give the *cis*-keto form in the singlet excited state.[1]

The dual phosphorescence spectra were observed in HBO and HBT at cryogenic temperature, indicating the existence of both the enol form and the *cis*-keto form in the triplet state.[2–6] However, at room temperature only the triplet enol form was observed by the triplet energy transfer from sensitizer to HBO.[7] Furthermore, the triplet state behavior of HBT has not been studied in detail, because HBT did not undergo intersystem crossing from the excited singlet state to the triplet state at room temperature.[8] Thus, the triplet state behavior of HBO and HBT is still quite obscure.

We have reported the novel effect of intramolecular hydrogen bonding on the triplet state behavior of organic compounds. For example, 2'-hydroxychalcone underwent one-way cis→trans isomerization assisted by adiabatic intramolecular hydrogen atom transfer in the triplet state.[9] In addition, we have succeeded in observing the triplet states of benzylideneaniline derivatives by introduction of the hydroxy group capable to form intramolecular hydrogen bonding and to induce hydrogen atom transfer in the triplet state.[10]



X = O : HBO, S : HBT

This paper aims to shed light on the effect of hydrogen bonding and hydrogen atom transfer on the triplet state behavior of HBO and HBT at room temperature mainly based on the laser photolysis experiments. Figure 1 shows the transient absorption spectra observed on benzophenone and Michler's ketone sensitization of HBO and HBT at room temperature under argon atmosphere in benzene.[11] These transient absorption spectra were quenched by oxygen with the rate constant of 3×10^9 M^{-1} s^{-1}. The triplet energy transfer takes place within the duration of the laser pulse and just after the laser pulse we can observe the triplet state of HBO and HBT. The lifetime of the triplet state was determined to be 7.4 and 7.5 μs for HBO and HBT, respectively under argon atmosphere in benzene.

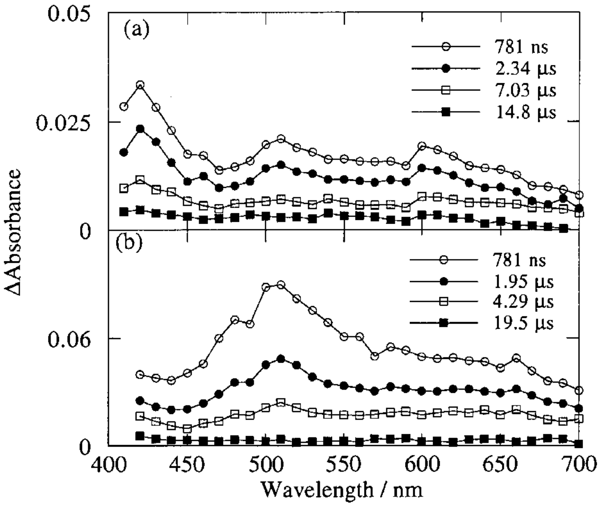


Figure 1. Trasient absorption spectra of HBO on benzophenone sensitization (a) and of HBT on Michler's ketone sensitization (b) in benzene under argon at room temperature.

The observed transient absorption spectra can be assigned to either the enol form or the *cis*-keto form in the triplet state. In order to clarify the structure of the observed transient spectra, we have studied the T–T absorption spectra of 2-(2-methoxyphenyl)benzoxazole (MBO) and 2-(2-methoxyphenyl)benzothiazole (MBT) as well as 2-phenylbenzoxazole (BO) and 2-phenylbenzothiazole (BT) as model compounds.

We should mention here the previously reported arguments about the lack of intersystem crossing for HBT and BT. Both HBO and HBT underwent hydrogen atom transfer to give the *cis*-keto form in the excited singlet state. The *cis*-keto form of HBT did not undergo intersystem crossing to the triplet state,[8] while HBO underwent intersystem crossing to the triplet state. It was reported that only a weak T–T absorption spectrum with a maximum at 420–440 nm was detected at room temperature on direct irradiation of BT.[12] Therefore, the lack of intersystem crossing in HBT was explained in connection with the low efficiency of intersystem crossing in BT by the importance of torsional motion around the single bond to the radiationless deactivation.[8,12] However, we have tried the laser flash photolysis of BT in benzene and have observed the T–T absorption spectra (λ_{max} = 400 nm) with quantum efficiency as high as 0.6. The T–T absorption spectra of BO, BT, MBO, and MBT observed at 10 μs after the laser pulse are shown in Figure 2. The lifetime under argon atmosphere was ca. 10 μs for all the compounds. The spectral profiles of MBO and MBT are similar to those of BO and BT and the absorption maximum appeared at 420 nm. However, the T–T absorption spectra of HBO and

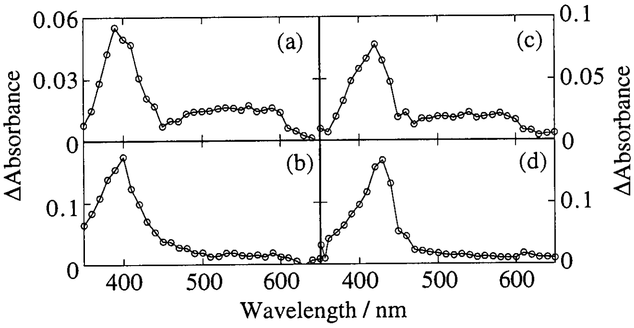


Figure 2. Transient absorption spectra of BO (a), BT (b), MBO (c) and MBT (d) in benzene under argon.

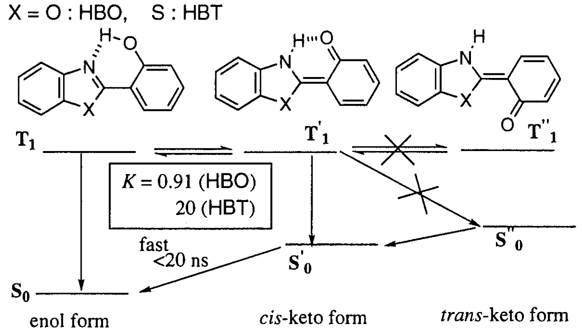


Figure 3. Potential energy diagram for hydrogen transfer in HBO and HBT.

HBT observed on triplet sensitization (Figure 1) are different from those of MBO and MBT (Figure 2) indicating that the observed triplet states for HBO and HBT are not simply the enol triplet, but the mixture of the enol form (^{3}E*) and the *cis*-keto form (^{3}K*).

We have tried to estimate the equilibrium constant (K = [^{3}K*]/[^{3}E*]) by measuring the rate constant of energy transfer from the transient species to several quenchers.[11] The quenching rate constants for the HBO triplet by *cis*- (E_T = 227 kJ mol^{-1}) and *trans*-stilbene (E_T = 206 kJ mol^{-1}) are determined to be 3.3×10^9 M^{-1} s^{-1} and 4.7×10^9 M^{-1} s^{-1}, respectively for HBO. The quenching rate constants for HBT by *cis*- and *trans*-stilbene are 3.2×10^8 M^{-1} s^{-1} and 1.7×10^9 M^{-1} s^{-1}, respectively and are lower than the values for HBO.

The triplet energies of the enol form and the *cis*-keto form for HBO are estimated to be 267 and 209 kJ mol^{-1} and those for HBT are estimated to be 248 and 206 kJ mol^{-1}, respectively from the phosphorescence spectra.[2,3] Thus, the triplet energies of the enol form of HBO and HBT are higher than those of *cis*- and *trans*-stilbene, while those of the *cis*-keto form are comparable to the triplet energy of *trans*-stilbene.

The observed quenching rate constants of HBT triplet by *trans*-stilbene as well as *cis*-stilbene are smaller than the diffusion controlled rate constant, while the values for HBO are nearly 1/2 of the diffusion controlled rate constant (k_{diff} = 6.3×10^9 M^{-1} s^{-1}). Since *cis*-stilbene can quench the triplet enol form with nearly the diffusion controlled rate constant, but can scarcely quench the triplet *cis*-keto form, we can estimate the equilibrium constant between the enol form and the *cis*-keto form (K = [^{3}K*]/[^{3}E*]) by using equation 1. Thus, K is estimated to be 0.91 and 20 for HBO and HBT, respectively.

As to the deactivation from the triplet state, one can expect

$$k_q = k_{diff}\,[^3E^*] / ([^3E^*] + [^3K^*]) = k_{diff} / (1 + K) \qquad (1)$$

the cis–trans isomerization of the *cis*-keto form to give the *trans*-keto form. If the *trans*-keto form was produced through the deactivation processes, one could observe its absorption spectra with the absorption maximum at 430 nm and the lifetime of 7.5 μs. However, we have observed only the T–T absorption spectra under oxygen atmosphere as well as argon atmosphere in benzene at room temperature. Therefore, the deactivation of the triplet state of HBO and HBT took place to give the enol form or the *cis*-keto form: the *cis*-keto form underwent fast reverse hydrogen atom transfer within our time resolution (~20 ns) to give the enol form. Thus, the diabatic as well as adiabatic cis–trans isomerization around the double bond in the *cis*-keto form did not take place in the triplet state. From these results, the potential energy surfaces of hydrogen atom transfer of HBO and HBT in the excited triplet state are depicted as shown in Figure 3.

In conclusion, we have found that HBO and HBT underwent hydrogen atom transfer to give the *cis*-keto form and have determined the equilibrium constant between the enol form and the *cis*-keto form in the triplet state.

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11 Laser photolyses were performed with 366 nm or 390 nm laser pulse by using an excimer laser (Lambda Physik LPX-100, XeCl, 308 nm) pumped dye laser (Lambda Physik FL-3002) with 5mJ/pulse and 10 ns fwhm. DMQ and QUI were used as laser dyes to obtain laser pulses of 366 and 390 nm, respectively. The concentration of HBO and HBT was adjusted to 0.01 M and that of benzophenone and Michler's ketone was adjusted to 0.03 and 0.006 M, respectively.
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