Direct Observation of the Photoinduced Hydrogen Atom Transfer in 2'-Hydroxychalcone

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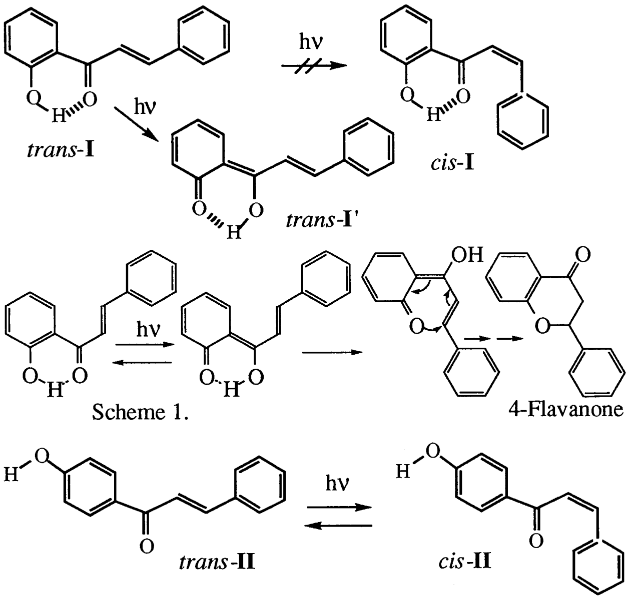
2'-Hydroxychalcone underwent intramolecular hydrogen atom transfer through the hydrogen bonding as revealed by the observation of the tautomer triplet state.

The photochemical behavior of 2'-hydroxychalcone (**I**) was previously studied.[1-3] **I** did not undergo trans-cis isomerization on photoirradiation.[2] The cyclization to form flavanone and flavone on irradiation under Ar with mercury lamp and under oxygen with laser has already been reported, although their quantum efficiencies seem to be very small.[1,3] As to the mechanism for the cyclization to form flavanone, Matsushima et al. proposed the intramolecular hydrogen atom transfer to give the tautomer followed by cyclization to form flavanone (Scheme 1). However, transient spectroscopies have not been studied in detail. We wish to report here a direct experimental finding that **I** would tautomerize by way of intramolecular hydrogen bonding based on the results obtained by laser transient spectroscopy.



Scheme 1.

On direct irradiation at 366 nm light by high pressure mercury lamp through glass filters **I** was stable and did not practically give any products such as cis isomers. However, 4'-hydroxychalcone **II**, which cannot form intramolecular hydrogen bonding, underwent mutual isomerization on photoirradiation.

On excitation by 308 nm excimer laser under Ar, **I** gave transient absorption spectra at ca. 400 and ca. 600 nm decaying with the lifetime of 1.2 μs in benzene (λ_{max}=410 nm and 610 nm) and 140 ns in methanol (λ_{max}=400 and 580 nm) as shown in Figure 1. The same transient spectra was observed on excitation of **I** in the presence of benzil (E_T=53.4 kcal mol^{-1})[4] as a triplet sensitizer exciting at 425 nm laser pulse. These transient spectra were quenched by oxygen in both solvents and were assigned to the T-T absorption spectrum; the quenching rate constant was determined to be 2.4×10^9 M^{-1} s^{-1} in benzene. The planar trans triplet states ($^3t^*$) and the perpendicular triplet states ($^3p^*$) are the candidates for the observed triplet states. The quenching rate constant by oxygen observed to be nearly 1/9 of the diffusion controlled rate constant in benzene (k_{dif}=(2-3)$\times 10^{10}$ M^{-1} s^{-1})[5] strongly indicates that the observed triplet state is the planar conformation.

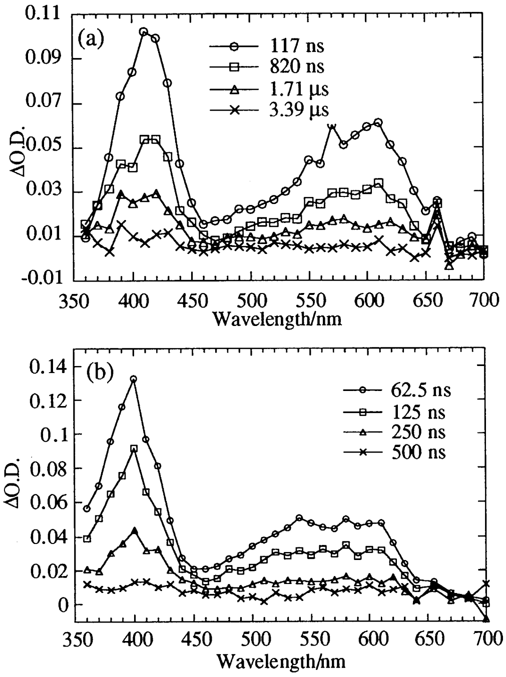


Figure 1. Transient absorption spectra observed on excitation of 2'-hydroxychalcone in benzene (a) and in methanol (b).

On excitation of **II** with 308 nm laser very weak transient spectra with λ_{max}=430 nm was observed both in benzene and in ethanol, which gave two decay components with 15 ns and 1.1 μs. Similar transient spectra were observed for chalcone with a shorter lifetime component (=13 ns)[6,7] and a longer lifetime component (=1.6 μs). Since the lifetime of the shorter component of **II** (15 ns) was almost the same as that of chalcone (13 ns), the shorter lifetime should be assigned to the triplet state of **II**. The longer components observed for **II** and chalcone were not quenched by oxygen, indicating that the longer components are not the excited triplet state but are the ground state derived from the intramolecular or intermolecular processes.

Since the lifetime of the observed T-T spectra of **I** was much longer than the reported chalcones[7] and no isomerization around the double bond was observed, we may propose that the observed transient for **I** was assigned to the triplet state, the conformation of which might be different from *trans*-**I**, such as a tautomer *trans*-**I**'.

In order to estimate the triplet energies of *trans*-**I** and the observed triplet state on excitation of *trans*-**I**, we did the quenching experiments. On laser excitation at 425 nm benzil triplets were quenched by *trans*-**I** with the rate constant of 5.0×10^8 M^{-1} s^{-1}. In our experimental condition benzil triplets were quenched by anthracene (E_T=42 kcal mol^{-1})[4] with the rate constant of 6.3×10^9 M^{-1} s^{-1}, and therefore, the diffusion-controlled rate constant (k_{dif}) is estimated as 6.3×10^9 M^{-1} s^{-1}. The quenching rate constant indicates that the quenching process of benzil triplet by *trans*-**I** should be the endothermic process with ca. 1.5 kcal mol^{-1} as estimated by eq. 1, where ΔE_a is the triplet energy difference between benzil and *trans*-**I**.[8] Therefore, the triplet energy of *trans*-**I** was estimated to be ca. 55 kcal mol^{-1}.

$$kq = k_{dif} \exp(-\Delta E_a/RT)/[1+\exp(-\Delta E_a/RT)] \qquad (1)$$

The triplet energy of the transients observed on laser photolysis of *trans*-**I** was estimated by the similar manner. The T-T absorption spectra of **I** observed on benzil sensitization with 425 nm laser pulse were quenched by anthracene with the rate constant of 1.7×10^9 M^{-1} s^{-1}. However, they were not quenched by pyrene (E_T=48.1 kcal mol^{-1})[4] up to the concentration of pyrene to be 3.8×10^{-3} mol dm^{-3}. Therefore, the triplet energy of the transient observed from *trans*-**I** is much lower than that of pyrene and should also be lower than that of anthracene by 0.5 kcal mol^{-1}, which was estimated from the quenching rate constant and eq. 1. The triplet energy of *trans*-**I'** was thus estimated to be 41.5 kcal mol^{-1}.

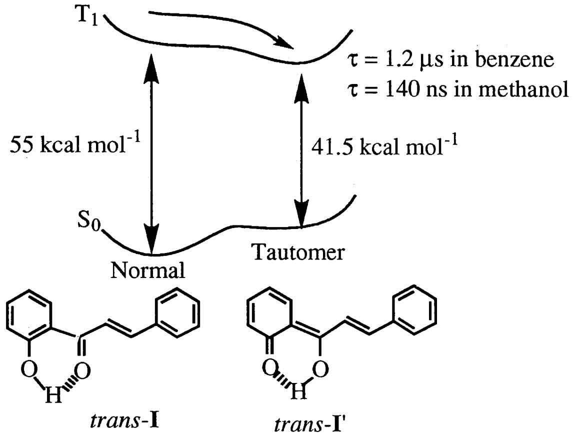


Figure 2. Potential energy surface of photoinduced hydrogen atom transfer in 2'-hydroxychalcone in the excited triplet state.

If the observed transient were assigned to the triplet state of the starting conformer *trans*-**I**, the two quenching experiments should give similar triplet energies. However, the energy transfer from the benzil triplet to *trans*-I gave the triplet energy of 55 kcal mol^{-1}, while the energy transfer from the triplet state *trans*-**I** to anthracene gave the triplet energy of 41.5 kcal mol^{-1}. Thus, the observation of the long lived triplet state and the difference in estimated triplet energies between the two experiments strongly indicate the occurence of the photoinduced hydrogen atom transfer in *trans*-**I** to give the tautomer *trans*-**I'** (Figure 2).

Finally, we should mention the absence of isomerization around the C=C double bond in *trans*-**I**. The triplet energy of the tautomer *trans*-**I'** is lower than that of the normal form and is similar to the value of one-way isomerizing olefins such as anthrylethenes and thus, *trans*-**I'** should undergo only cis→trans isomerization.[9] Therefore, we propose the lack of photochemical isomerization in **I** is the consequence of the hydrogen atom transfer to give the tautomer triplet state, where the planar trans conformation does not undergo twisting around the double bond but only deactivates to the ground state.

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References and Notes

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