Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-8212299. We thank Professor Julian L. Roberts, Jr., of the University of Redlands, for assistance with the kinetic measurements.

Registry No. *cis*-CHCl=CHCl, 156-59-2; $CH_2{=}CCl_2$, 75-35-4; CHCl=CCl_2, 79-01-6; $CCl_2{=}CCl_2$, 127-18-4; (*p*-ClPh)$_2$C=CCl_2, 72-55-9; superoxide ion, 11062-77-4; *trans*-1,2-dichloroethene, 156-60-5; chloroethene, 75-01-4; aldrin, 309-00-2; dieldrin, 60-57-1.

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Transient Absorption Study of the Intramolecular Excited-State and Ground-State Proton Transfer in 3-Hydroxyflavone and 3-Hydroxychromone

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Nano- and picosecond fluorescence studies provide the reaction kinetics and relaxation in the excited-state proton transfer of the hydrogen bonding system.[1-5] The mechanism of the excited-state proton transfer in 3-hydroxyflavone was proposed by Sengupta and Kasha.[6] Recently, Itoh et al.[7] have reported time-resolved and steady-state fluorescence studies of the excited-state proton transfer in 3-hydroxyflavone (3-HF) and 3-hydroxychromone (3-HC), which lacks a phenyl group in γ-pyrone ring of 3-HF. They demonstrated that the excited-state proton transfer from the normal form (N*) to the tautomer (T*) takes place more rapidly in 3-HC than in 3-HF and suggested that the phenyl group has a large effect on the excited-state proton transfer and relaxation process of 3-HF. We present here a transient absorption study of the mechanism for proton transfer in the excited state (N* → T*) as well as in the ground state (T → N) of 3-HF and 3-HC at room temperature.

As reported in the previous paper,[7] the 3-methylpentane (MP) solutions of 3-HF and 3-HC show no normal form fluorescence but only the long-wavelength fluorescence at 500–530 nm. The long-wavelength fluorescence was ascribed to the radiative transition from T* to the corresponding ground state (T). However, the existence of this type of ground-state tautomer as an intermediate from T* to the ground-state normal form (N) has never been evidenced. The present transient absorption study reveals the mechanism and kinetics of the processes of T* → T → N as well as the absorption bands of T and T*. Further, the ground-state reverse proton transfer (T → N) was observed to take place more rapidly in 3-HC than 3-HF.

The MP solution of 3-HF shows the strong absorption spectrum in the 300–360-nm region. The ground-state absorption bleaching and recovery were observed in the 337-nm excitation of the MP solution at room temperature by using a N_2 laser (Molectron UV 12) and a flash lamp (USSI 3CP-3) system.[8] A single-exponential recovery of the absorption with a lifetime of 3.1 μs was observed. This long time recovery can be ascribed to either the recovery through the excited-state proton transfer followed by the reaction processes shown in Figure 1 or the decay of the triplet species. However, it is confirmed that the former process is predominant in the recovery of the ground-state absorption by the consistent decay of the transient absorption of T, as will be mentioned later.

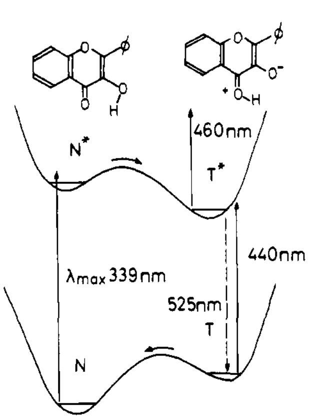

Figure 1. Schematic energy diagram of the proton transfer in 3-hydroxyflavone.

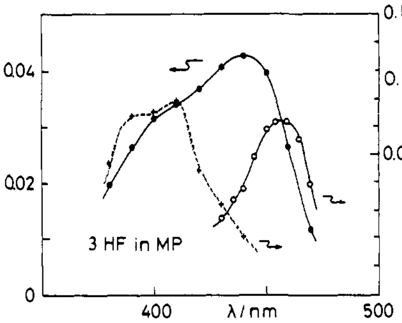

Figure 2. Time-resolved transient absorption spectra of the MP solution of 3-hydroxyflavone at room temperature: (●) depicted at 300-ns delay after a laser excitation; (○) at ~13-ns delay; (+) at ~50-ns delay.

The time-resolved absorption spectra of the aerated MP solution of 3-HF at 360–500 nm were determined as shown in Figure 2. The rather broad band (λ_{max}440 nm) was observed at 300-ns delay after a laser excitation. Further, a very short time decay absorption was observed at λ_{max} 460 nm. The transient absorption at 440 nm exhibits a single exponential decay (τ = 2.9 μs), while the lifetime at 460 nm is approximately 1–2 ns. Both lifetimes are almost invariant in the deaeration of solution. Therefore, the long- and short-lifetime absorption bands are not ascribed to the triplet species. The long time absorption may be attributable to the ground-state tautomer (T), since the lifetimes of T* and N* were reported to be less than 2 ns and several 10 ps, respectively. The decay time of this transient shows a good consistency with the ground-state recovery time of N. These findings demonstrate the experimental evidence of the reaction scheme of the excited-state proton transfer and relaxation process (Figure 1). The decay times of the 460-nm absorption band (Figure 2) and of the T* fluorescence are in good consistency with each other within experimental error, though the determination of the absorption lifetime has less accuracy than that of the fluorescence lifetime. Therefore, the absorption band at 460 nm is ascribed to the $S_n \leftarrow S_1$ absorption of T*.

On the other hand, the aerated MP solution of 3-HF shows a transient absorption at 390–420 nm in addition to the T* and T absorption bands. The lifetime of ~200 ns remarkably increases in the deaeration of the solution by nitrogen gas bubbling. Therefore the absorption band at 400 nm may be attributable to the triplet–triplet absorption band. Hamanoue et al.[9] reported triplet absorption bands of flavone at 365–370 and 640–650 nm and suggested it as the lowest triplet state with a π,π* character.[10]

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Since the spectrum may be shifted to the longer wavelength region from that of flavone by the electronic effect of 3-hydroxy group, the triplet–triplet absorption band at 390–420 nm may be ascribed to the triplet state of 3-HF ($^3N^*$). The 2-methyltetrahydrofuran solution of 3-HF exhibits transient absorption spectra similar to those of the MP solution, though neither the $S_n \leftarrow S_1$ absorption spectrum of T* nor bleaching of the ground-state absorption could be observed because of a strong background from fluorescence due to T* and N*.

Transient absorption spectra of the aerated MP solution of 3-HC were observed at 380–400 and 400–450 nm. The decay times are ~90 and ~400 ns, respectively. By analogy to the spectra of 3-HF, the former and latter absorption bands may be ascribed to the triplet-triplet absorption of N* and the transient absorption of T, respectively. It is noteworthy that the decay time of T is significantly smaller in 3-HC than 3-HF. This means that the ground-state proton transfer from T to N occurs more rapidly in 3-HC than 3-HF. This fact suggests that the effect of phenyl group in 3-HF on the ground-state proton transfer is analogous to that observed for the excited-state process, as reported in the previous paper.

Acknowledgment. We are indebted to Dr. P. F. Barbara for supplying a copy of his paper[5] prior to publication.

Registry No. 3-HF, 577-85-5; 3-HC, 13400-26-5.

Sequential Mechanism in the Oxidative Demetalation of a Trimethylenemethane–Fe(CO)$_3$ Complex, Tricarbonyl[(1-3,6-η)-2-methylenecyclopentane-1,3-diyl]iron

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A crucial problem in the chemistry of transition metal–hydrocarbon complexes such as those of cyclobutadiene (CBD)[1] and trimethylenemethane (TMM)[2] concerns the extent and duration of the influence of the metal when the ligand is oxidatively[1,2a] or photochemically[2b] "liberated" and trapped by olefins or acetylenes. A general mechanism for such processes is shown in Scheme I, where O and G represent oxidizing and capture agents, respectively. The present paper uses the known properties[3-5] of 2-alkylidenecyclopentane-1,3-diyls as criteria by which to judge whether the metal influences the behavior of the TMM intermediate 2-methylenecyclopentane-1,3-diyl (1) generated from an

1

iron complex. The results indicate a sequential mechanism and provide the first direct evidence of the liberation of a metal-free TMM in its ground triplet spin state in such reactions.

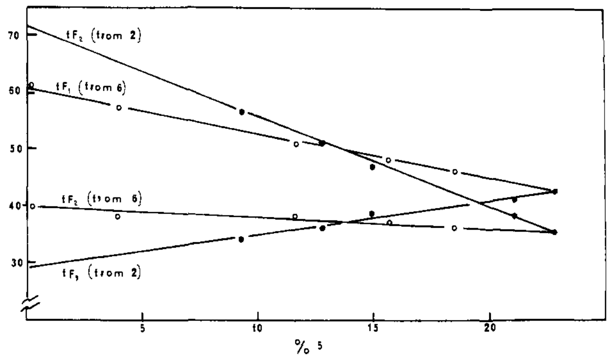
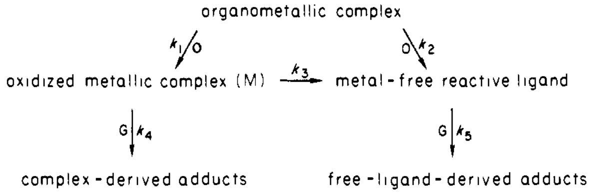
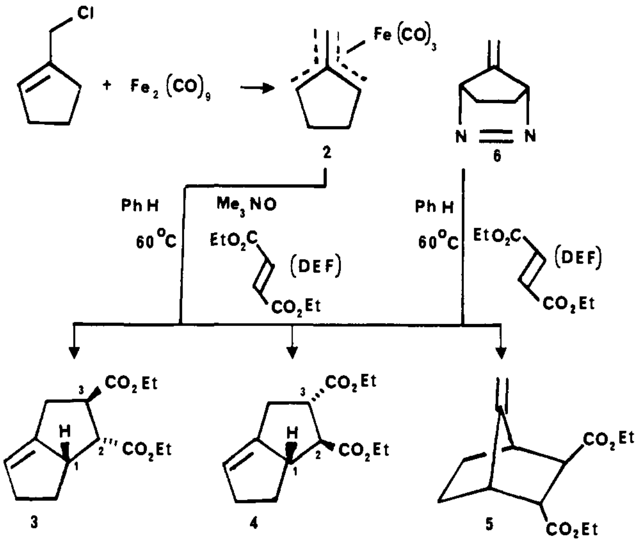


Figure 1. Least-squares fit to linear form of the percent of each trans-fused adduct (tF) as a function of trans-bridged adduct (5) in the thermal and oxidative decompositions of diazene 6 and complex 2, respectively, at 60 °C in benzene solution in varying concentrations of diethyl fumarate (DEF).

Scheme I



Scheme II



The title complex 2,[6] isolated in 3% yield as a yellow liquid by gas chromatography (GC), was prepared by heating cyclopent-1-enylmethyl chloride[7] and Fe$_2$(CO)$_9$ at reflux in degassed benzene under argon for 12 h.[8] Oxidation of 0.03 M 2 with carefully dried trimethylamine-*N*-oxide[9] (2–3 M) in benzene solution at 60 °C gave a 14% yield of a mixture of hydrocarbon products, at least ten of which were empirically dimers of 1. When the oxidation of 2 was carried out in the presence of a large excess of diethyl fumarate (DEF), two fused cycloadducts, 3[6] and 4,[6] designated tF$_1$ and tF$_2$ or vice versa according to their retention time on GC, and the trans-bridged adduct 5[6] were observed (Scheme II) in combined yields ranging from 9% to 19%.[10] The same three products were obtained from diazene 6 (96% yield) as was established by comparisons of GC retention times and spectroscopic properties of isolated materials.

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(6) Characterized by elemental composition, mass spectrometric molecular weight, and spectroscopic properties.

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(10) The yield of CO$_2$ was 0.22 mol/mol of 2. If only one CO ligand/mol of 2 is required to be oxidized to CO$_2$ to effect formation of the cycloadducts 3–5, the observed cycloadduct yield would correspond to 42–87%. Control experiments established that the product ratios were kinetically determined and did not change during prolonged reaction times.

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