Hydrogen-Atom Abstraction from the Solvent by the Lowest Excited Triplet State of Chromone Yielding the β-Keto-Type Solvent Adduct(s)

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The lowest excited triplet state of chromone with mixed $n\pi^*$-$\pi\pi^*$ character abstracts a hydrogen atom from the solvent. Although the ketyl-type radical thus generated is indistinguishable from the β-enol-type radical, this radical (or its keto form, i.e., the β-keto-type radical) gives rise to formation of the β-keto-type solvent adduct(s).

By measurements of the chemically induced dynamic electron polarization (CIDEP) signals upon nanosecond laser photolysis of chromone in 2-propanol, Igarashi et al.[1] concluded that the carbonyl oxygen atom of the $n\pi^*$ triplet state and the β-carbon atom of the $\pi\pi^*$ triplet state abstracted a hydrogen atom from the solvent generating the ketyl-type radical and a small amount of the α-keto-type radical, respectively; when tri-*n*-butyltin hydride was added, enhanced generation of the latter radical was ascribed to hydrogen-atom abstraction from the additive. Since this observation seems to be a typical example demonstrating the character-dependent photochemistry of excited triplet states and it is generally believed that the order of $n\pi^*$ and $\pi\pi^*$ triplet energy levels can sometimes be changed by changing the solvent polarity, the present paper deals with the behavior of triplet chromone in 3-methylpentane (a nonpolar solvent) and ethanol (a polar solvent)..

Chromone (Aldrich) was recrystallized three times from diethyl ether (Merck), GR-grade 3-methylpentane (Wako) was purified by passing it through an alumina column and spectral-grade ethanol (Nacalai) was dried using a molecular sieve 3A (Wako). All the sample solutions were degassed by several freeze-pump-thaw cycles and the phosphorescence spectra were recorded using a Hitachi MPF-4 spectrophosphorimeter. Nanosecond laser photolysis was performed using the 266-nm light pulse with a full width at half-maximum intensity of 5 ns from a Nd^{3+}:YAG laser and the transient absorption spectra were recorded by a multichannel analyzer;[2] the decay curves of transient absorptions and phosphorescences were analyzed by means of a combination of a photomultiplier (Hamamatsu R329 or R928) with a storage oscilloscope (Iwatsu TS-8123).

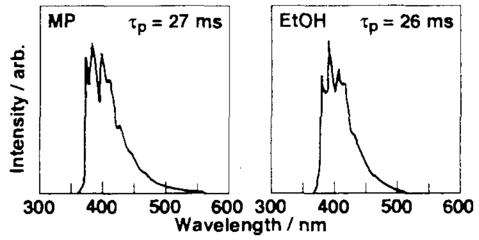


Figure 1. Phosphorescence spectra and their lifetimes (τ_p) obtained for chromone at 77 K in MP and EtOH.

The phosphorescence spectra and their lifetimes (τ_p) obtained for chromone at 77 K in 3-methylpentane (MP) and ethanol (EtOH) are shown in Figure 1. Similar phosphorescence spectra are also obtained in methylcyclohexane (τ_p=23 ms), 2-methyltetrahydrofuran (τ_p=26 ms), EPA (diethyl ether/isopentane/ethanol=5:5:2 in volume ratio, τ_p =28 ms) and ME (methanol/ethanol=1:1 in volume ratio, τ_p=28 ms). It thus can be concluded that the lowest excited triplet state of chromone is of mixed $n\pi^*$-$\pi\pi^*$ character irrespective of the solvent polarity. This is based on the well-known fact that an $n\pi^*$-type phosphorescence spectrum generally exhibits a clear progression of the carbonyl vibration and has a short lifetime on the order of a few milliseconds.[3-5]

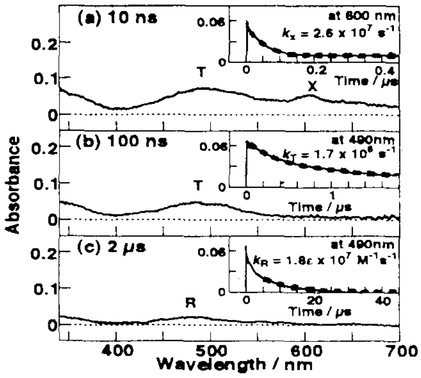
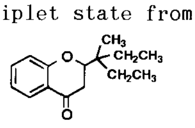


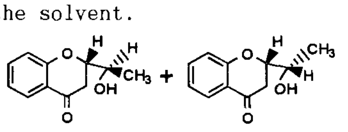
Figure 2. Transient absorption spectra and decay curves of transient absorptions (——) obtained by nanosecond laser photolysis of chromone at room temperature in MP. The dashed curve is best-fit one calculated by the first-order (with rate constant k_X or k_T) or second-order (with rate constant k_R) decay kinetics; for k_R, ε is the absorption coefficient of a transient species different from the lowest excited triplet state of chromone.

Figure 2 shows the transient absorption spectra and the decay curves of transient absorptions obtained by nanosecond laser photolysis of chromone at room temperature in MP: Although the spectrum obtained at the end of pulse excitation, i.e., at 10 ns delay, has bands T and X, the former band can safely be assigned to the triplet-triplet absorption originating from the lowest excited triplet state of chromone; this is based on the fact that the lifetime (τ_T=28 ms) of band T obtained at 77 K in EPA is equal to the phosphorescence lifetime (τ_P=28 ms) stated previously. After the rapid single-exponential disappearance of band X with rate constant k_X, band T decreases to a constant absorbance following the first-order decay kinetics with rate constant k_T and then band R disappears following the second-order decay kinetics with rate constant k_R; for k_R, ε is the absorption coefficient of a transient species different from the lowest excited state of chromone. Similar results with $k_T=3.1\times10^6$ s^{-1} and $k_R=3.6\varepsilon\times10^7$ M^{-1} s^{-1} are obtained in EtOH, but determination of k_X is impossible owing to the rapid disappearance of band X. In MP, the decay rate constant ($k_X=2.6\times10^7$ s^{-1}) of band X is one order of magnitude greater than that ($k_T=1.7\times10^6$ s^{-1}) of band T and no intensity increment of band T can be seen during the decrement of band X. This suggests that band X is the absorption due to a transient species (**TRN**) generated from the lowest excited singlet state of chromone. In fact, sub-picosecond laser photolysis reveals that bands X and T appear simultaneously with a rise time of 20 ps in EtOH. Since steady-state photolysis of chromone gives no evidence reflecting formation of a product from **TRN**, its definitive identification can not presently be given.

As reported previously,[6] ^{1}H-NMR analysis for the products obtained by steady-state photolysis of chromone in MP and EtOH at room temperature indicates formation of the following β-keto-type solvent adducts (**adduct 1** and **adducts 2**, respectively). Furthermore, the lowest excited triplet states of aromatic carbonyl compounds such as benzophenone,[7] 4-chromanone[6] and flavanone[6] abstract a hydrogen atom from the solvent, and recombination of two ketyl radicals thus generated yields the pinacols. For chromone, therefore, band R shown in Figure 2c can be ascribed to the absorption due to the radical species generated by hydrogen-atom abstraction of the lowest excited triplet state from the solvent.



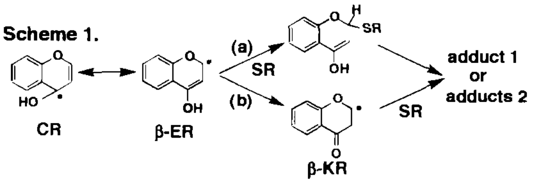
adduct 1



adducts 2

In summary, we conclude as follows: (1) Although Igarashi et al.[1] proposed the coexistence of $n\pi^*$ and $\pi\pi^*$ excited triplet states in 2-propanol, no such an evidence has been obtained. (2) Only the lowest excited triplet state of mixed $n\pi^*$-$\pi\pi^*$ character abstracts a hydrogen atom from the solvent generating the solute (**CR**) and solvent (**SR**) radicals. (3) As shown in Scheme 1, **CR** (the ketyl-type radical) thus generated is indistinguishable from the β-enol-type radical (β-**ER**) owing to the planar π-conjugation of all the atomic *2p* orbitals concerned, but a large reactivity of the latter radical compared with the former radical may result in the following consecutive reactions; (a) recombination of β-**ER** with **SR** followed by enol→keto conversion [or (b) enol→keto conversion of β-**ER** to the β-keto-type radical (β-**KR**) followed by recombination with **SR**] yields **adduct** 1 or **adducts 2**.

Scheme 1.



Formation of **adduct** 1 (or **adducts** 2) can not be ascribed to recombination of **SR** with the α-keto-type radical as was reported by Igarashi et al.[1] Furthermore, it is confirmed that addition of tri-*n*-butyltin hydride does not affect the time-dependent change of transient absorption spectra but accelerates the triplet decay as well as formation of **adduct** 1 (or **adducts** 2). Since these results indicate that the lowest excited triplet state of chromone abstracts a hydrogen atom from both the solvent and the additive generating β-**ER** initially, the α-keto-type radical assigned by Igarashi et al.[1] might be β-**KR** formed by enol→keto conversion of β-**ER** (cf. Scheme 1b). If this is true, addition of basic tri-*n*-butyltin hydride may assist β-**ER**→β-**KR** conversion resulting in observation of the CIDEP signals responsible for only the latter radical.

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