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Journal of Photochemistry and Photobiology A: Chemistry 111 (1997) 35–39

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

A comparison of the photochemistry of flavanone with that of flavone originating from their lowest excited triplet states in ethanol

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Received 6 May 1997; received in revised form 28 July 1997; accepted 5 August 1997

Abstract

By means of nanosecond laser photolysis and steady-state photolysis at room temperature, it is concluded as follows: (1) Both the lowest excited triplet states of flavanone and flavone with mixed nπ*–ππ* character abstract a hydrogen atom from ethanol generating the solute and solvent radicals. (2) The radical species of flavanone is undoubtedly its ketyl radical yielding the pinacol-type isomers and the solvent adduct. (3) The ketyl radical of flavone is indistinguishable from the enol-benzyl-type radical but the photoproducts formed from the latter radical (or from the corresponding keto-benzyl-type radical) are obtained. © 1997 Elsevier Science S.A.

Keywords: Flavanone; Nanosecond laser photolysis; Ketyl radical; Flavone

1. Introduction

For aromatic carbonyl compounds with two nearby excited triplet states of nπ* and ππ* character, it is generally believed that the order of triplet energy levels is sometimes changed by substitution of molecules or changing the solvent polarity [1–6]. In connection with this, Matsushima et al. [7] have reported that the lowest excited triplet state of flavanone is of ππ* character in benzene (a non-polar solvent) or of nπ* character in 2-propanol (a polar solvent), yielding 2'-hydroxychalcone or the coupling products (the pinacol-type isomers and the solvent adduct) respectively. For flavone in 2-propanol, furthermore, Sakaguchi et al. [8] have proposed generation of two kinds of solute radicals depending on the nature of additives (the hydrogen-atom donors), i.e. hydrogen-atom abstraction of triplet nπ* flavone from xanthene generates the ketyl radical and that of triplet ππ* flavone from tri-*n*-butyltin hydride (or sodium borodeuteride) generates the β-keto-type radical, i.e. the keto-benzyl-type radical.

For anthraquinone and β-haloanthraquinones [9,10], benzophenone [11–13] and indanone [14], however, we have concluded that their lowest excited triplet states are of nπ* or mixed nπ*–ππ* character even in a strong hydrogen-bonding solvent such as 2,2,2-trifluoroethanol; in the usual solvents, all the lowest excited triplet states are of nπ* character irrespective of the solvent polarity. As an extension of our studies on the photophysics and photochemistry of aromatic carbonyl compounds, therefore, the present paper deals with the lowest excited triplet states of flavanone (a benzopyranone compound) and flavone (a benzopyrone compound) generating their radical species by hydrogen-atom abstraction from ethanol. The phosphorescence spectra and their lifetimes measured for flavanone and flavone at 77 K reveal that the lowest excited triplet states are of mixed nπ*–ππ* character irrespective of the solvent polarity. Although this suggests that both the lowest excited triplet states of flavanone and flavone at room temperature abstract a hydrogen atom from ethanol, the results obtained by nanosecond laser photolysis and steady-state photolysis are as follows. (1) For flavanone, the pinacol-type isomers and the solvent adduct formed from the ketyl radical are obtained. (2) For flavone, compound **1** and isomers **2a**, **2b** formed from the enol-benzyl-type or keto-benzyl-type radical are obtained (cf. Schemes 1 and 2).

2. Experimental details

Flavanone (Aldrich) and EP-grade flavone (Wako) were recrystallized three times from *n*-pentane. The solvents used were ethanol, EPA (diethyl ether:isopentane:ethanol = 5:5:2 in volume ratio) and 3-methylpentane. Although Uvasol diethyl ether (Merck) was used without further purification,

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PII S1010-6030(97)00235-9

GR-grade isopentane and 3-methylpentane from Wako were purified by passing them through an alumina column and spectral-grade ethanol (Nacalai) was dried using a molecular sieve 3A (Wako) preheated in a crucible over a Bunsen burner and cooled in vacuo. All the sample solutions were degassed by several freeze–pump–thaw cycles.

Nanosecond laser photolysis was performed using the fourth harmonic (the 266 nm light pulse with a full width at half-maximum intensity of 5 ns) from an Nd^{3+}:YAG laser (Continuum Surelight I) and the transient absorption spectra were recorded using a multichannel analyzer composed of a polychromator (Unisoku M200), an image intensifier (Hamamatsu V3347U) and a linear position-sensitive detector (Unisoku USP501) controlled by a microcomputer (NEC PC-9801RA) [15]; the decay curves of phosphorescences and transient absorptions were analyzed by means of a combination of a photomultiplier (Hamamatsu R329 or R928) with a storage oscilloscope (Iwatsu TS-8123).

The phosphorescence spectra at 77 K were recorded using a Hitachi MPF-4 spectrophosphorimeter and the absorption spectral change upon steady-state photolysis at room temperature was recorded using a Hitachi 200-20 spectrophotometer; steady-state photolysis was carried out using the 313 nm monochromatic light selected from a USH-500D super-high-pressure mercury lamp.

3. Results and discussion

The lowest excited triplet state of benzophenone is of typical $n\pi^*$ character with a lifetime of 5.7 ms in EPA, 5.0 ms in 2-methyltetrahydrofuran (MTHF) or 5.3 ms in methylcyclohexane (MCH), and the phosphorescence spectrum exhibits a clear progression of the carbonyl vibration [11]. In contrast, as shown in Fig. 1, the phosphorescence spectra and their lifetimes (τ_P) obtained for flavanone and flavone in ethanol (EtOH), EPA and 3-methylpentane (MP) at 77 K are greatly different from those obtained for benzophenone. Similar results are also obtained in ME (methanol: ethanol = 1:1 in volume ratio), MTHF and MCH at 77 K, but no substantial solvent polarity effects on the shapes of phosphorescence spectra (and the phosphorescence lifetimes) can be seen. Since all the phosphorescence decay curves can well be reproduced by single-exponential functions and no long-lived decay components can be seen, we propose that the lowest excited triplet states of flavanone and flavone are of mixed $n\pi^*$–$\pi\pi^*$ character irrespective of the solvent polarity. Hence, the much longer phosphorescence lifetimes obtained for flavone than those obtained for flavanone may reflect that the $\pi\pi^*$ nature for the lowest excited triplet state of the former compound is large compared with that of the latter compound; for ring-substituted valerophenones, however, an equilibrium polulations of the $n\pi^*$ and $\pi\pi^*$ triplet states is proposed by Wagner et al. [6].

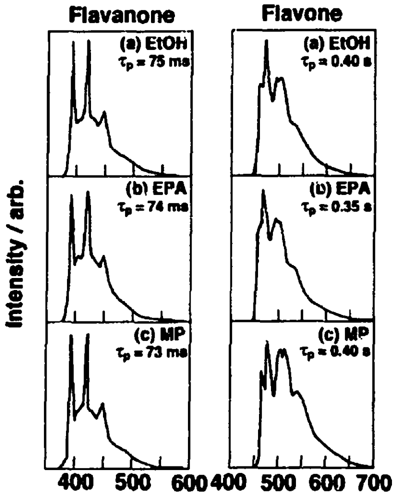


Fig. 1. Phosphorescence spectra and their lifetimes (τ_P) obtained for flavanone and flavone in EtOH, EPA and MP at 77 K.

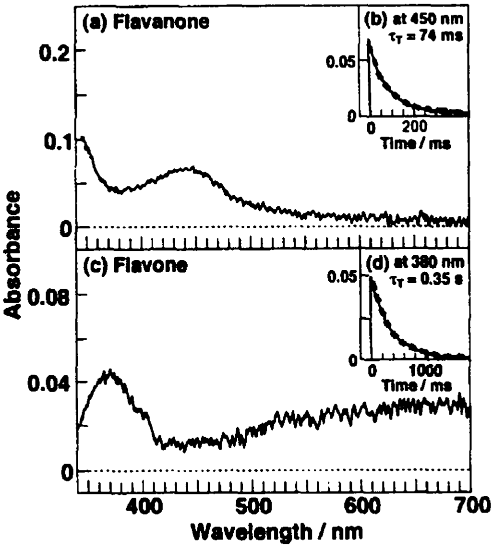


Fig. 2. (a), (c) $T' \leftarrow T_1$ absorption spectra and (b), (d) their decay curves (——) obtained by nanosecond laser photolysis of flavanone and flavone in EPA at 77 K. In (b) and (d), the dashed curves are single-exponential functions with lifetimes (τ_T) indicated.

As shown in Fig. 2, nanosecond laser photolysis of flavanone and flavone in EPA at 77 K gives rise to the appearance of transient absorption spectra which decrease with time following single-exponential functions with lifetimes (τ_T) equal to the phosphorescence lifetimes (τ_P). Hence, the transient absorption spectra shown in Fig. 2(a), (c) can safely be assigned to the triplet–triplet ($T' \leftarrow T_1$) absorptions originating from the lowest excited triplet states of flavanone and flavone respectively.

Fig. 3 shows the transient absorption spectra obtained by nanosecond laser photolysis of flavanone and flavone in

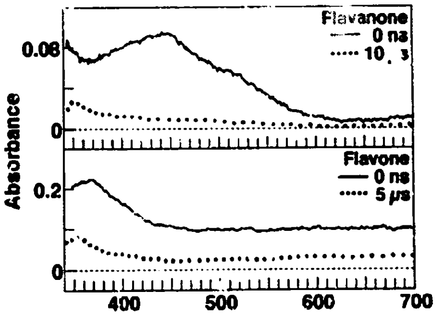


Fig. 3. Transient absorption spectra obtained by nanosecond laser photolysis of flavanone and flavone in EtOH at room temperature.

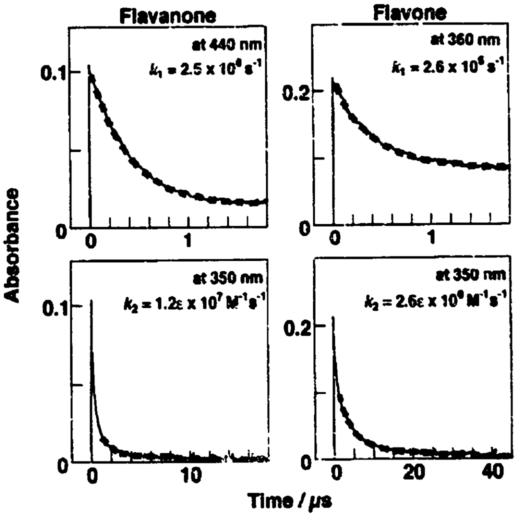


Fig. 4. Decay curves of transient absorptions (——) obtained by nanosecond laser photolysis of flavanone and flavone in EtOH at room temperature. The dashed curves are best-fit curves calculated by the first-order decay kinetics with rate constants k_1 or the second-order decay kinetics with rate constants k_2. For k_2, ϵ is the absorption coefficient of a transient species different from the lowest excited triplet state of flavanone or flavone.

EtOH at room temperature. Although the spectra (solid lines) obtained at the end of pulse excitation, i.e. at 0 ns delay, are identical with the $T' \leftarrow T_1$ absorption spectra shown in Fig. 2(a), (c), the spectra (dotted lines) obtained at longer delays are somewhat different from the $T' \leftarrow T_1$ absorption spectra. In accordance with this, as shown in Fig. 4, the transient absorptions (appearing within the duration of pulse excitation) decrease with time following the first-order reaction kinetics with rate constants k_1 and then the second-order reaction kinetics with rate constants k_2; for k_2, ϵ is the absorption coefficient of a transient species different from the lowest excited triplet state of flavanone or flavone.

Fig. 5 shows the absorption spectral changes upon steady-state photolysis of flavanone and flavone in EtOH at room temperature. Clearly, the photochemical reaction of the former compound is somewhat different from that of the latter compound and the results obtained by ^{1}H NMR analysis of the final products are as follows [16]. (1) For flavanone, the pinacol-type isomers and the solvent adduct are formed in accordance with the result obtained in 2-propanol by Matsushima et al. [7]. Although they have reported that the lowest excited triplet state of flavanone in benzene (a non-polar solvent) is of ππ* character and undergoes bond cleavage of the pyranone ring yielding 2′-hydroxychalcone, the results obtained in MP (a non-polar solvent) by us are found to be identical with those obtained in EtOH (a polar solvent); we thus propose that 2′-hydroxychalcone is formed from the lowest excited singlet state of flavanone on the basis of the facts that the photochemistry of flavanone in benzene is not affected by the presence of air and the identical result is also obtained even in aerated EtOH or MP. (2) For flavone, however, a reduced compound (**1**) and two coupling isomers (**2a** and **2b**) are formed in a ratio of **1**:**2a**:**2b** = 1:2.2:2 (cf. Scheme 1).

All the results obtained so far can be summarized as follows. (1) The lowest excited triplet states of flavanone and flavone with mixed nπ*–ππ* character abstract a hydrogen atom from the solvent generating the corresponding ketyl and solvent radicals. (2) For flavanone, the second-order decay of transient absorption responsible for the ketyl radical (**KR**)

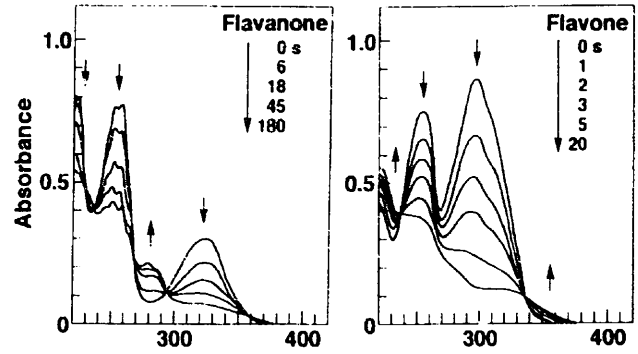
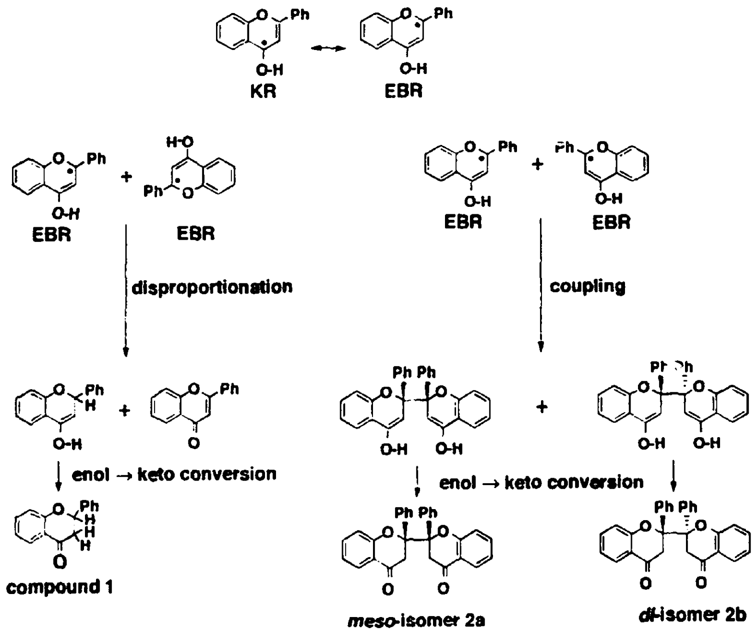
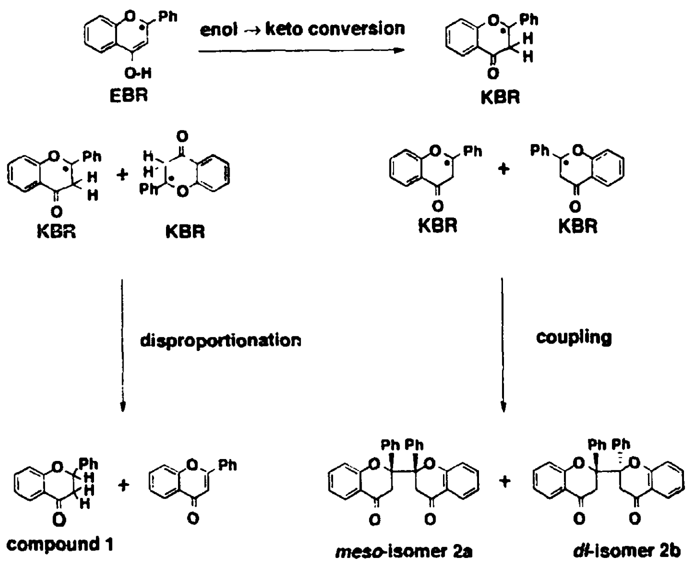


Fig. 5. Absorption spectral changes upon steady-state photolysis of flavanone and flavone in EtOH at room temperature.



Scheme 1.



Scheme 2.

reflects recombination of two **KR** yielding the pinacol-type isomers (and that of **KR** with the solvent radical yielding the solvent adduct); this result is consistent with that obtained for benzophenone [17], although its lowest excited triplet state is of $n\pi^*$ character. (3) For flavone, **KR** is indistinguishable from the enol-benzyl-type radical (**EBR**) owing to the planar π-conjugation of all the atomic 2p orbitals concerned, but formation of compound **1** (and isomers **2a**, **2b**) can be ascribed to the following consecutive reactions: (a) disproportionation (and coupling) of two **EBR** followed by enol → keto conversion (cf. Scheme 1), or (b) enol → keto conversion of **EBR** to the keto-benzyl-type radical (**KBR**) followed by disproportionation (and coupling) of two **KBR** (cf. Scheme 2).

By means of a chemically induced dynamic electron polarization (CIDEP) technique applied for flavone in 2-propanol, as stated previously, Sakaguchi et al. [8] have concluded that the α-carbon atom of the $\pi\pi^*$ triplet state abstracts a hydrogen atom from the additive (tri-*n*-butyltin hydride or sodium borodeuteride) generating the β-keto-type radical, i.e. the keto-benzyl-type radical (**KBR**). In comparison with the reactivity of acrolein or butadiene as a model compound, however, hydrogen-atom abstraction as proposed by Sakaguchi et al. may be generally improbable. We thus propose that **EBR → KBR** conversion is assisted by the presence of additives (tri-*n*-butyltin hydride and sodium borodeuteride) resulting in observation of the CIDEP signals responsible for only the keto-type radical (**KBR**), i.e. the enol → keto conversion stated above may be affected by the basic character of the additive. Experimental work along this line as well as investigation of the photochemistry of flavanone originating from its lowest excited singlet state are in progress.

Acknowledgements

This work was supported by a Grant-in-Aid for Priority-Area-Research on Photoreaction Dynamics from the Ministry of Education, Science, Sports and Culture of Japan (No. 06239101).

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