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Photo-antioxidant abilities of 2-hydroxybenzoyl compounds

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Abstract

Plastics are indispensable for our comfortable life. But, they are easily degraded by autoxidation, especially under the action of UV light, due to their organic character. Therefore, additives preventing the photo-oxidation are needed. 2-Hydroxybenzophenones are widely used as ultraviolet absorbers (UVA), and their effect is discussed in many papers. However, there are few papers, in which the effect of substituents on the benzene nucleus and/or the 2-hydroxybenzoyl group on the photo-antioxidant ability is directly examined. This study focuses on clarifying such substituent effect. As a result, it has been made clear that the photo-antioxidant ability is better improved by introducing a substituent into *p*-position than *m*-position of the 2-hydroxyl group. In addition, it was found that the photo-antioxidant ability is enhanced by enlarging the conjugation system of the group bonded to the 2-hydroxybenzoyl carbonyl group. The substituent effect activity of (2-hydroxybenzoyl)-benzene is also discussed.

Keywords: UVA; 2-Hydroxybenzophenone; 2′-Hydroxyacetophenone; 2-Hydroxybenzoyl; Substituent effect

1. Introduction

In recent years, UV intensity at ground level is increasing, due to depletion of the ozone layer. UV radiation is well known to promote the degradation of polymer materials, such as plastics. Ultraviolet absorbers (UVA), therefore, are very important as one of the additives to prevent plastics from photo-degradation by UV.

The UV absorbers include benzophenone type, triazole type, and triazine type compounds. Among them, the benzophenone-type UVA, because of its simplest structure, have been frequently studied not only as polymer additives [1–4], but due to the importance of their photochemistry [5–7].

They absorb UV to be in the excited state, but release some heat to return to the original ground state. This functional mechanism is characterized by an intramolecular hydrogen transfer. Such a mechanism is based on the first finding by Waller [8] that large Stokes shifts occur in fluorescence spectra of salicylic acid and its ester. The shift was explained by the hydrogen transfer, in the first singlet excitation state, driven by the change of acidities of the hydroxyl group of phenol and the carbonyl group in excited and ground states. The discovery shows that many compounds having 2-hydroxybenzoyl moiety do the hydrogen transfer on absorbing UV. The mechanism is studied energetically using molecular orbital method [9–11], fluorescence and UV spectra [7,12]. Thus, many studies have been reported about the photo-stabilization mechanism of 2-hydroxybenzoyl compounds. However, the substituent effect on UV absorption characteristics and photo-antioxidant activities of 2-hydroxybenzoyl compounds has not been studied. In this study, such a substituent

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effect of 2-hydroxybenzoyl groups as well as an effect of the moiety bonded to the 2-hydroxybenzoyl were examined on photo-antioxidant activities of 2-hydroxybenzoyl compounds.

2. Experimental

2.1. Materials-UV absorbers (UVA)

2′-Hydroxy-4′-chloroacetophenone was purchased from Lancaster Synthesis Ltd. 2-Hydroxybenzophenone, 2,4′-dihydroxybenzophenone, 2,4-dihydroxybenzophenone, and 2-hydroxy-4-methoxybenzophenone were purchased from Tokyo Kasei Kogyo Co, Ltd. 2-Hydroxy-5-chlorobenzophenone and 2-hydroxy-5-bromobenzophenone were purchased from Aldrich. These commercial compounds were used after recrystallisation.

2′-Hydroxychalcone, 2-hydroxy-5-methoxybenzophenone, and 2′-hydroxy-4′-chloroacetophenone were synthesized according to a general Friedel–Crafts reaction. 2′-Hydroxy-4′-methylacetophenone, 2′-hydroxy-4′-ethylacetophenone, 2′-hydroxyisobutyrophenone, 2-hydroxy-4′-chlorobenzophenone, 2-hydroxy-4-chlorobenzophenone, and 2-hydroxy-4-methylbenzophenone were also synthesized by a general procedure of a Fries rearrangement [13]: the esters of starting materials being synthesized using various well known esterification reactions. 2′-Hydroxyacrylophenone was synthesized via a Mannich reaction on 2′-hydroxyacetophenone [14]. 2′-Hydroxy-2-chloroacetophenone [15] and 2-hydroxy-4′-methylbenzophenone [16] were synthesized by a procedure described in a corresponding paper. 2′-Hydroxy-5′-acetoxyacetophenone, 2′-hydroxy-4′-acetoxyacetophenone, 2-hydroxy-4′-acetoxybenzophenone, and 2-hydroxy-4-acetoxybenzophenone were synthesized by the reaction of the corresponding dihydroxyacetophenone or dihydroxybenzophenone with acetic anhydride. 2′-Hydroxy-4′-benzyloxyacetophenone, 2-hydroxy-4′-benzyloxybenzophenone, 2-hydroxy-4-benzyloxybenzophenone, and 2-hydroxy-4′-methoxybenzophenone were also synthesized by the reaction between benzyl bromide or methyl iodide and dihydroxyacetophenone or dihydroxybenzophenone.

Two new compounds, 2-hydroxy-4′-acetoxybenzophenone and 2-hydroxy-4′-benzyloxybenzophenone, were identified as follows.

2-Hydroxy-4′-acetoxybenzophenone (yellow plate crystals): yield: 3.4%, mp: 65.9–66.5 °C; ^{1}H NMR ($CDCl_3$, TMS): 12.0 ppm (1H, *OH*), 7.9–6.9 ppm (8H, *phenyl*), 2.4 ppm (3H, CH_3). FT-IR (KBr): 1761 cm^{-1} (CH_3–*COO*–C_6H_4), 1624 cm^{-1} (*ortho* *CO*–C_6H_4–OH), 1332 cm^{-1} (CH_3COO), 1220 cm^{-1} (C_6H_4–*OH*), 854 cm^{-1} (1,4-substituted benzene), 759 cm^{-1} (1,2-substituted benzene).

2-Hydroxy-4′-benzyloxybenzophenone (yellow plate crystals): yield: 32.9%, mp: 86.1–86.6 °C; ^{1}H NMR ($CDCl_3$, TMS): 12.7 ppm (1H, *OH*), 7.6–6.4 ppm (8H, *phenyl*), 5.1 ppm (2H, CH_2). FT-IR (KBr): 1624 cm^{-1} (*ortho* *CO*–C_6H_4–OH), 1257 cm^{-1} (C_6H_4–*O*–CH_2), 1230 cm^{-1} (C_6H_4–*OH*), 794 cm^{-1} (1,4-substituted benzene), 789 and 704 cm^{-1} (mono-substituted benzene), 750 cm^{-1} (1,2-disubstituted benzene).

2.2. Measurement of photo-antioxidant ability

An air-tight reaction system was used including a transducer detecting a minute differential pressure. Azo-bis-isobutylonitrile (AIBN) of 2.0×10^{-2} M in chlorobenzene was used as an initiator and a 2.0 M solution of styrene in chlorobenzene, as substrate. Photo-oxidation was carried out at 50 °C under irradiation with UV light (high-pressure mercury-vapour lamp) above 290 nm. The relative oxidation rate (%) was calculated based on the oxidation rate in absence of an additive.

3. Results and discussion

3.1. Substituent effect in benzene ring of 2-hydroxybenzoyls

2-Hydroxylbenzoyls have a carbonyl group at the *o*-position to the hydroxyl group, and both groups can form a six-membered ring by hydrogen bonding. The effect of substituents connected to either the benzene ring or the carbonyl was investigated, in order to know the influence of the substituents on photo-antioxidant ability.

3.1.1. Photo-antioxidant ability of 2′-hydroxyacetophenone derivatives

The effect of substituents on the benzene ring of 2-hydroxybenzoyls was studied using 2′-hydroxyacetophenone as standard, because the methyl group is considered to show little substituent effect in comparison with another group: the Taft substituent constant of methyl being 0. The R_1 is a substituent introduced on *p*-position of the hydroxyl group. Shown in Table 1 is the relationship between photo-antioxidant ability and ultraviolet absorption ability in terms of R_1 substituents. The σ_p, here, is a Hammett substituent constant of the *p*-position. It is seen from the table that λ_{max}'s are red-shifted, compared with that of 2′-hydroxyacetophenone, regardless of the kind of substituents. It is also clear that the photo-antioxidant ability is enhanced with the increase in ε. This result agrees well with a general concept that the higher ε is, the better is the photo-antioxidant ability. That is to say, a *p*-position substituent is found directly to influence UV absorption character of 2-hydroxybenzoyl compounds.