

Confirmation of photo Fries rearrangement of phenyl salicylates using an on-line ultra violet radiation/pyrolysis-GC/MS system

A. Hosaka¹, Y. Sakamoto¹, C. Watanabe¹ and Y. Ohkatsu²

¹ Frontier Laboratories Ltd., Koriyama, Japan

² Kogakuin University, Shinjuku-ku, Japan

Abstract

Although salicylate ultraviolet absorbers (S-UVA) have been widely used, their underlying mechanism has not been fully established. In this study, using a new developed ultraviolet irradiation/pyrolysis GC/MS system, the correlation between photo-Fries rearrangement and photo-antioxidant ability was examined with five S-UVA having various chemical structures. The obtained results showed that the photo-Fries rearrangement does not seem responsible for photo-antioxidant of S-UVA.

Keywords

phenyl salicylates, ultra violet absorber, photo-Fries rearrangement, on-line ultra violet radiation/pyrolysis-GC/MS

1. Introduction

Ultraviolet light absorbers play a key role in improving weatherability of polymer materials. Phenyl salicylate ultraviolet absorbers (S-UVA) have been extensively used on account of excellent compatibility with and little coloration against a variety of resins, as well as high synergism with hindered amine light stabilizers. Several papers report the photo-antioxidant activity of S-UVA including, for example, (1) change of photo energy to thermal energy by intramolecular hydrogen transfer reaction and more (2) photo-antioxidant activity based on the formation of benzophenone by Fries rearrangement. However, in these photo-antioxidant activity mechanisms, the importance by photo-Fries rearrangement has not been investigated in detail, but its clarification is considered necessary for molecular design of new S-UVA. In this investigation, a new developed online ultraviolet irradiation/pyrolysis-GC/MS system (UV/Py-GC/MS) was used to analyze products generated by photo-Fries rearrangement of various S-UVA, and to determine the relative generation rates of the products. This result was compared that of photo-antioxidant ability of S-UVA.

2. Experimental

2.1 S-UVA

Table 1 shows five S-UVA used in this study including their physical data.

2.2 Photo-Fries rearrangement

Figure 1 shows a UV/Py-GC/MS system used in this study to measure the Fries rearrangement. The system can irradiate UV light, which is transmitted through an optical fiber cable from UV light source (deuterium lamp), onto a sample cup placed in temperature-controlled heating furnace. A thin film sample (ca. 5mg) was formed by solvent evaporation over the bottom of the sample cup (4 mm i.d, 8 mm high, 0.1 mm wall thickness) with two openings of 1 mm i.d, for helium flow at upward, and was irradiated for 30 min to several hours at about 50°C under helium atmosphere. Photo-Fries rearrangement products and starting materials were separated and analyzed by GC/MS qualitatively and [quantitatively](#).

2.3 Photo-oxidation

Styrene was photo-oxidized under UV light irradiation (high-pressure Hg lamp) with and without S-UVA, and the photo-antioxidant ability of S-UVA was determined, as relative oxidation rate; 100% means no inhibition and 0% means complete inhibition.

3. Results and discussion

3.1 Relative generation rate of photo-Fries rearrangement products

Figure 2 shows the results of photo-Fries rearrangement with S-UVA. The chromatogram of each sample shows unreacted S-UVA as the main peak. S-UVA1, S-UVA2 and S-UVA5 also show photo-Fries rearrangement products, while S-UVA3 and S-UVA4 do not produce photo-Fries rearrangement products. Figure 3 shows the formation amount of photo-Fries rearrangement products of S-UVA1 with time. The peak

area of each product increased linearly with time until 1 hour of reaction time. Therefore, the formation amount after 30 min of reaction time can be used as the measure of photo-Fries rearrangement rate. Table 2 summarizes the photo-Fries rearrangement rates. S-UVA1 exhibits the largest rate of photo-Fries rearrangement, and 30min irradiation gives 15.5% rearrangement. On the other hand, S-UVA2 and S-UVA5 show less rearrangement respectively, and the amount of reaction products was found to be 20.2% and 56.0% based on S-UVA1, and S-UVA3 and S-UVA4 show no rearrangement.

3.2 Comparison of photo-Fries rearrangement rates with photo-antioxidant ability.

Table 2 also shows photo-antioxidant ability of five S-UVA. S-UVA2 with a methoxy group shows the highest photo-antioxidant ability of 76.1%, whereas the nitro substituted gives the least effect on photo-antioxidant ability. Comparing these results with the corresponding photo-Fries rearrangement rates reveals that there is no correlation between both parameters. In other words, one with the highest photo-antioxidant ability underwent only a small percentage of photo-Fries rearrangement. These results suggest that the photo-Fries rearrangement does not seem responsible for photo-antioxidant of S-UVA.

Table 1 Series of S-UVA samples

Sample	Chemical Name	Structure	λ max (nm) ^{※1}	ϵ ^{※1}
S-UVA 1	phenyl salicylate		311.0	5100
S-UVA2	phenyl 5-methoxysalicylate		333.5	6820
S-UVA3	4-nitrophenyl salicylate		312.5	6400
S-UVA4	4-tert-butylphenyl salicylate		311.0	5020
S-UVA5	phenyl 5-methylsalicylate		321.5	4740

※1 solvent: CH₂Cl₂ (5 x 10⁻⁵M)

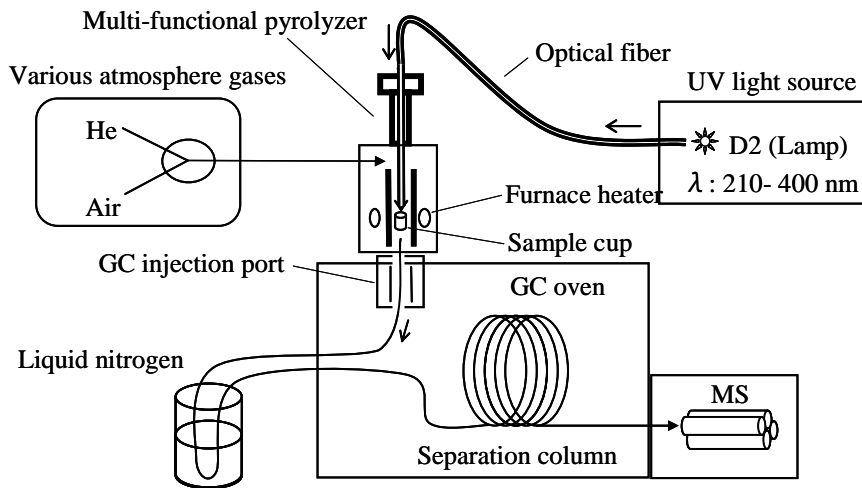


Figure 1 Configuration of on-line UV/PY - GC/MS system for analyzing photo, thermal, and oxidative degradation products generated by UV irradiation

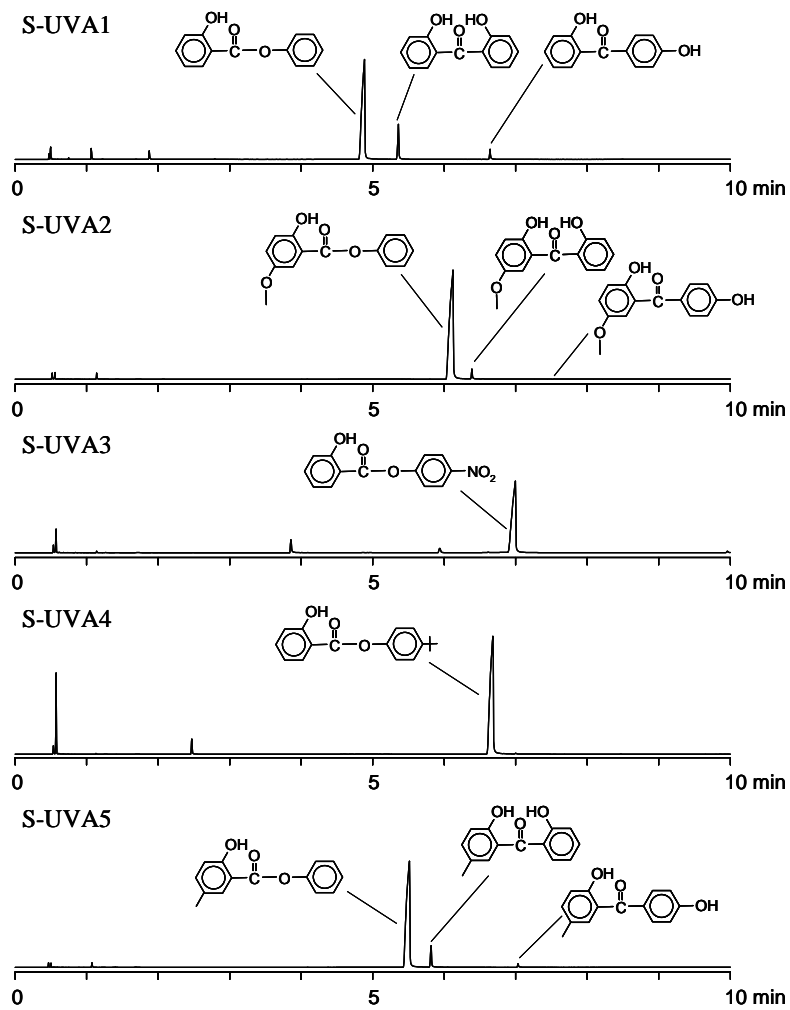


Figure 2 GC chromatograms of S-UVAs after UV irradiation for 30 min at He flow atmosphere

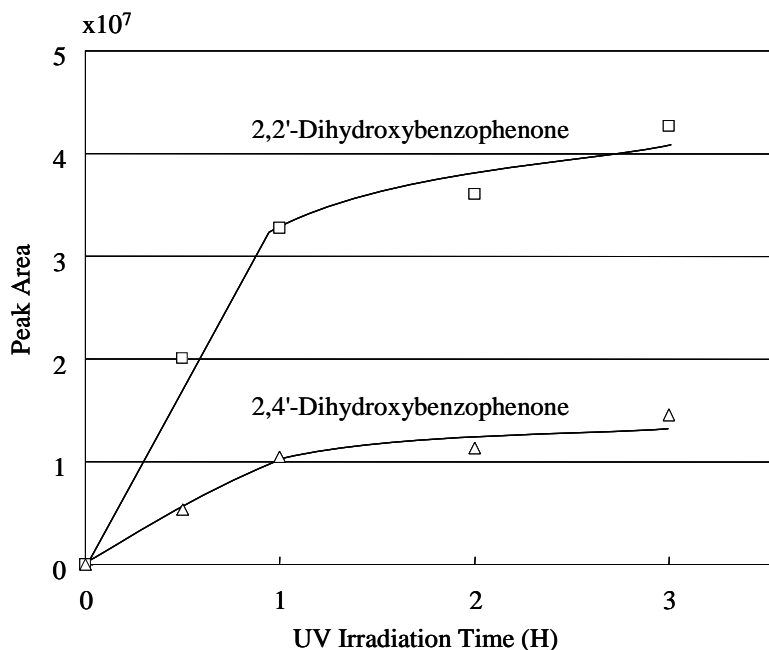


Figure 3 Relationship between irradiation time and amount of products generated from photo-Fries rearrangement reaction of phenyl salicylate

Table 2 Comparison of relative oxidation rate and relative generation rate of S-UVAs

Sample No.	Relative generation rate (%) ※1	Relative oxidation rate (%) ※2
no additive	-	100
S-UVA1	100.0	86.5
S-UVA2	20.2	76.1
S-UVA3	0.00	100.0
S-UVA4	0.00	83.1
S-UVA5	56.0	93.7

※1 reaction time: 30min

※2 [styrene]=2.0M, [AIBN]=10⁻²M, [additive]=10⁻⁴M in chlorobenzene at 50°C