

Photo-Fries rearrangement of phenyl salicylate studied by two-dimensional infrared spectroscopy[☆]



Hideyuki Shinzawa^{*}, Yuki Matsumoto, Seiji Tsuzuki, Yukihiro Shimoi, Hiroyuki Suda

National Institute of Advanced Industrial Science and Technology (AIST), Japan

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ABSTRACT

Photo-Fries rearrangement of phenyl salicylate was examined by real-time infrared (IR) monitoring in conjunction with density functional theory (DFT) calculation. Changes in the spectral features were readily captured during the photo-induced chemical reaction of the phenyl salicylate by means of two-dimensional (2D) correlation spectroscopy. The obvious variations of spectral intensities due to the production of 2,2'-dihydroxybenzophenone and 2,4'-dihydroxybenzophenone are clearly identified to provide in-depth understanding to the photo-Fries rearrangement. Namely, when exposed to UV-irradiation, the majority of the phenyl salicylate undergoes photothermal degradation. Further irradiation to the rest of the phenyl salicylate then results in the production of 2,2'-dihydroxybenzophenone followed by the development 2,4'-dihydroxybenzo-phenone products. Such delay in the production of 2,4'-dihydroxybenzo-phenone implies the presence of some more pathways, which makes its reaction efficiency lower than that of 2,2'-dihydroxybenzophenone.

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1. Introduction

Spectroscopic process monitoring of a chemical reaction is an analytical tool of practical interest. In particular, vibrational spectroscopy has been used for monitoring several chemical reaction processes by taking advantage of characteristic spectral changes due to consumption and production of chemical components in systems [1–6]. For example, each chemical functional group in a molecule vibrates at a unique frequency, providing a specific peak in spectrum. Steady variation of peak intensity observed in spectra thus can be used as useful indicator for the consumption or generation of chemical component during the reaction. Infrared (IR) spectroscopy is well suited for the in situ monitoring of chemical reaction process, particularly those carried out under the irradiation of UV light [7–12].

The photo-Fries rearrangement involves the transformation of molecules such as phenolic esters to hydroxy aryl ketones. This chemical reaction is important since the molecules generated by the rearrangement can be used as source for photoresist materials. Fig. 1 shows a schematic illustration of the reaction which occurs when an aromatic polyester is subjected to UV irradiation. The

aromatic polyester first undergoes main-chain cleavage by free radical reaction and then subsequent multiple rearrangements to develop ortho-hydroxy ketone [13–15]. Initial interest in the photo-Fries rearrangement of aromatic polyesters was mainly due to the fact the reaction is accompanied by the formation of ortho-hydroxy aromatic compounds with great photostability, while the total amount of the reaction products are relatively small [14]. A considerable amount of attention has also been paid to the photo-Fries rearrangement of polymer pendant groups. It is also known that the rearrangements of some aromatic polyester are often incomplete and result in the formation of both the ortho and the para-hydroxyphenone rearranged products. For example, the photo-Fries rearrangement of phenyl salicylate generates major product (2,2'-dihydroxybenzophenone) and minor product (2,4'-dihydroxybenzophenone) as shown in Fig. 2 [13]. Unfortunately, the details of the reaction mechanism has not been fully understood yet.

In this work, the first two-dimensional (2D) IR correlation spectra of the photo-Fries rearrangement are reported to demonstrate how the technique can elucidate the details of the reaction mechanism [16,17]. Namely, the photo-Fries rearrangement of phenyl salicylate was examined by IR spectroscopy to capture the evolutionary change induced by the reactions. The time-resolved IR spectra collected during the early stage of the photo-Fries rearrangement process are then subjected to 2D correlation spectroscopy. Density functional theory (DFT) calculation was also carried out to support the assignments of IR bands. The 2D

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^{*} Corresponding author.

E-mail address: h-shinzawa@aist.go.jp (H. Shinzawa).

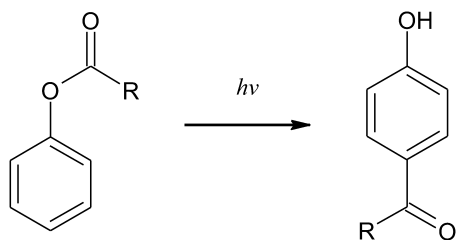


Fig. 1. Schematic illustration of a photo-Fries rearrangement.

correlation analysis of the time-dependent IR spectra reveals the subtle but important changes in the spectral intensities which are not readily identified in the stuck of the 1D spectra, e.g., the occurrence of several variations of the phenyl salicylate, including photothermal degradation as well as development of photo-Fries reaction products. Of note is that the result clearly suggested the IR intensity change of 2,2'-dihydroxybenzophenone predominantly occurs before that of 2,4'-dihydroxybenzophenone. Such delay in the spectral intensity variation mostly suggests that the minor products undergoes even more reaction pathways during the photo-Fries reaction.

2. Theory

2.1. DFT calculation

All the DFT calculations of geometry optimization and vibrational analysis were carried out with the Gaussian 09 package [18] at the B3LYP/6-311G(d,p) level of the theory. Before the geometry optimizations by the DFT calculations, stable conformations were searched by using CONFLEX program [19] with the MMFF94 force field [20]. It was confirmed that the optimized structures have no imaginary frequencies by the DFT calculations. The frequency scaling factor 0.9682 reported by Merrick et al. [21] was used for the vibrational analysis.

3. Experimental

3.1. IR measurement

Phenyl salicylate was provided by Wako Pure Chemical Industries, Ltd., and used without further purification. A schematic illustration of the experimental set-up is shown in Fig. 3. A Graseby Specac Golden Gate diamond attenuated total reflectance (ATR) accessory with pressure control (Specac. Ltd., Orpington, UK) was aligned in the external sample compartment of a PerkinElmer

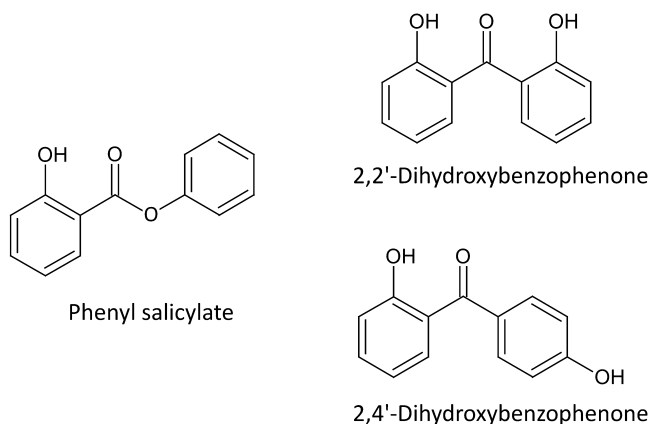


Fig. 2. Molecular structures of phenyl salicylate, 2,2'-dihydroxybenzophenone, 2,4'-dihydroxybenzophenone.

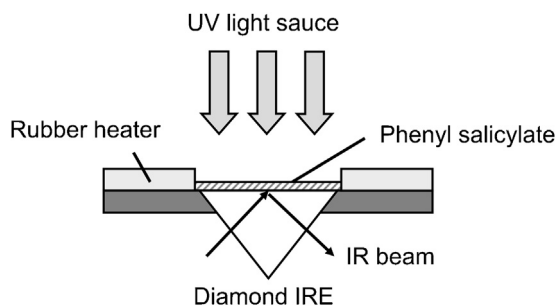


Fig. 3. Schematic illustration of IR monitoring of the photo-Fries rearrangement.

Spectrum 100 spectrometer equipped with a TGS detector. A silicon rubber heater (OM heater, Aichi, Japan) was placed around the diamond internal reflectance element (IRE). The 5 mg phenyl salicylate powder was placed on the surface of the IRE and compressed at 5 MPa by the pressure applicator to provide close contact with the IRE. After the removal of the pressure applicator, UV light was irradiated with an external UV irradiation equipment (AS ONE, Osaka, Japan). In our geometry, the UV intensity was approximately 50 mW/cm². During the UV irradiation, time-dependent IR spectra of the phenyl salicylate was collected every 10 min by co-adding 64 scans. The measurements were carried out at 60 °C.

4. Results and discussion

4.1. 2D correlation analysis of time-dependent IR spectra

Fig. 4 illustrates the time-dependent IR spectra of phenyl salicylate over the (A) 1720–1660 cm⁻¹ and (B) 970–890 cm⁻¹ regions, respectively. The corresponding second derivative spectra are also provided in Fig. 4(C) and (D) for references. A broad peak observed in Fig. 4(A) and (C) represents an IR band arising from the carbonyl groups of the phenyl salicylate [22]. The gradual decrease in the IR spectral intensity in this region implies photothermal degradation which eventually results in the weight loss of the sample. In fact, such oxidation phenomena is often predominantly observed in the photo-induced variation of some aromatic polyesters since the efficiency of the photo-Fries reaction itself is relatively low [14]. Consequently, it is most likely that the phenyl salicylate substantially undergoes photothermal degradation as well as photo-chemical reactions when exposed to the UV light. On the other hand, the steady increase in the spectral intensity observed around at 935 cm⁻¹ in Fig 4(B) and (D) suggests the development of reaction product. While such evolutionary feature of the spectral intensity probably represents the reaction product arising from either photo-Fries reaction or photothermal degradation, unfortunately, the origin of the IR band is not fully understood yet.

(A) Synchronous and (B) asynchronous correlation spectra derived from the time-dependent IR spectra of the phenyl salicylate are shown in Fig. 5, respectively. The 2D correlation spectra illustrate correlation intensity between two different IR regions, e.g., 1720–1660 cm⁻¹ and 970–890 cm⁻¹. The synchronous correlation spectrum provides one negative correlation peak at the coordinate (1685, 935). The negative correlation indicates that the consumption of the phenyl salicylate is compensated with the emerging contribution from some components. The asynchronous correlation spectra show a specific negative correlation peak in the corresponding region. The development of the asynchronous correlation peak in this region is particularly important. The decrease in the spectral intensity at 1685 cm⁻¹ predominantly occurs before the increase that at 935 cm⁻¹. In other words, the

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