



# Photoreductive transformation of fluorinated acetophenone derivatives on titanium dioxide: Defluorination vs. reduction of carbonyl group

Shigeru Kohtani\*, Takuya Kurokawa, Eito Yoshioka, Hideto Miyabe\*

Department of Pharmacy, School of Pharmacy, Hyogo University of Health Sciences, 1-3-6, Minatogima, Chuo-ku, Kobe 650-8530, Japan

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## ABSTRACT

Photoreductive transformation of mono- and di-fluoromethyl acetophenone (AP) derivatives on the P25 titanium dioxide (TiO<sub>2</sub>) has been studied in deaerated ethanol solution under UV irradiation. 2-Monofluoromethyl AP (MFAP) was stable in the dark and existed as keto form in ethanol, whereas 64% of 2,2-difluoromethyl AP (DFAP) transformed into hemiketal form (photocatalytically inactive form) under the same condition. Under the UV irradiation with the TiO<sub>2</sub> particles, the reduction of MFAP afforded only the defluorinated ketone, while the reduction of DFAP provided not only defluorinated ketones but also a hydrogenated alcohol. The reduction of carbonyl group and defluorination of DFAP concurrently occurred on TiO<sub>2</sub>, in which the formation of MFAP was observed as an intermediate of the sequential defluorinations. These two parallel reactions were initiated by electron transfer from the surface defect sites (Ti<sub>sd</sub>) to DFAP adsorbed on the TiO<sub>2</sub> surface. A possible reaction mechanism for DFAP is proposed and discussed on the basis of thermodynamic data upon the C–F bond cleavage of anion radical species generated during the photocatalysis.

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## 1. Introduction

Photocatalysis on semiconductors is defined as a light-driven redox reaction at a solid/liquid or a solid/gas interface. In particular, photocatalysis is a unique catalytic methodology compared to the conventional thermal or photochemical reactions because a sequential multi-step electron transfer induced by accumulated electrons and holes on surface of semiconductors can initiate some characteristic reactions. This property makes it possible to be utilized in water splitting [1,2], reduction of carbon dioxide [2,3], synthetically useful organic reactions [3–5] and so on. It is well known that titanium dioxide (TiO<sub>2</sub>) can accumulate electrons at defective trap sites (Ti<sub>sd</sub>) on the surface under UV photoexcitation [6–8]. The accumulated electrons have been used for the sequential multi-step electron transfer in the reduction of substrates adsorbed on TiO<sub>2</sub>, for example, hydrogenations of alkenes and alkynes [3,9], aromatic nitro compounds [3–5], aldehydes and ketones [3,4] etc. The electron accumulation on Ti<sub>sd</sub> has been physicochemically investigated by means of electron paramagnetic

resonance [10,11], photoacoustic [12,13], photoluminescence [14] and diffuse reflectance IR [15] or UV–vis spectroscopy [16].

We have recently demonstrated that the P25 TiO<sub>2</sub> exhibited the excellent photocatalytic activity to hydrogenate several aromatic carbonyl compounds into corresponding alcohols under the combination of UV light irradiation and deaerated conditions in ethanol [17]. We have further examined the adsorptive and kinetic behaviors on the reductive hydrogenation of AP derivatives, and found that conduction band (CB) electrons or those trapped at the Ti<sub>sd</sub> on TiO<sub>2</sub> actually take part in the photohydrogenation [18]. We have also found that most of the reaction rates depend on the reduction potentials ( $E_{red}$ ) of substrates and proposed that a sequential two-step electron transfer leads to the hydrogenation reaction [19]. However, contrary to our expectation, the hydrogenation rate for 2,2,2-trifluoroacetophenone (TFAP) having an electro-withdrawing trifluoromethyl group was much slower than that for AP, though  $E_{red}$  for TFAP is sufficiently positive compared to that for AP [18]. The photo-hydrogenation of TFAP followed the first-order rate law because of the predominant formation of ketal or hemiketal as inactive species in ethanol, i.e., only a few percent of TFAP remained in the original keto form as active species [18]. Thus, the formation of ketal or hemiketal for TFAP in ethanol greatly affects the kinetics on the photocatalysis.

\* Corresponding authors. Fax: +81 78 304 2858.

E-mail addresses: [kohtani@huhs.ac.jp](mailto:kohtani@huhs.ac.jp) (S. Kohtani), [miyabe@huhs.ac.jp](mailto:miyabe@huhs.ac.jp) (H. Miyabe).

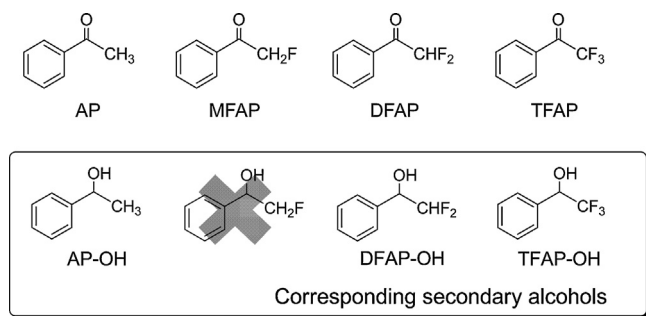


Fig. 1. AP derivatives and corresponding secondary alcohols.

Fluorine containing compounds are often used for pharmaceutical and agrochemical reagents. Since the C–F bond is one of the strongest bonds, the C–F bond activation/cleavage is a field of current interest in organic chemistry [20], though less is known about the catalytic methods. Photocatalytic reaction is one of the promising ways to induce the C–F bond activation/cleavage for such fluorinated compounds under mild conditions. Kaprinidis and Turro reported photosensitized defluorination of saturated perfluorocarbons in the presence of various photosensitizing amines [21]. Burdeniuc et al. also reported photoinduced catalytic defluorination of perfluoroalkanes to give perfluoroalkenes using decamethylferrocene [22] and mercury [23] as photosensitizers. Moreover, photocatalytic defluorination of fluorinated substrates has been examined using some semiconductor photocatalysts such as CdS [24], ZnS [24,25], metal-doped ZnS [26], and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> [27]. In general, these semiconductors used for the defluorination reactions possess high CB energy. On the contrary, TiO<sub>2</sub> does not have such a high CB level. Therefore, TiO<sub>2</sub> has not been regarded as an active photocatalyst for the C–F bond activation/cleavage.

In this paper, we report the photoreductive transformation of mono- and di-fluoromethyl AP derivatives including C–F bond cleavage upon the UV irradiated P25 TiO<sub>2</sub>. The structures of these compounds are summarized in Fig. 1. We have already reported that the photocatalytic reaction of AP and TFAP gives only the hydrogenated alcohols such as 1-phenylethanol (AP-OH) and 1-phenyl-2,2,2-trifluoroethanol (TFAP-OH) without defluorination, respectively. Andrieux et al. reported that the electrochemical reduction of 2-fluoromethylacetophenone (MFAP) has yielded AP via the reductive defluorination [28]. Therefore, we expect that the photocatalytic reduction of MFAP on TiO<sub>2</sub> may afford the defluorinated ketone. Moreover, it is interesting to note whether the reaction of 2,2-difluoromethylacetophenone (DFAP) with two fluorine atoms provides the hydrogenated alcohol of 1-Phenyl-2,2-difluoroethanol (DFAP-OH) or the defluorinated ketone. In this paper, we also propose a possible mechanism for the reduction of DFAP and discuss the reaction route on the basis of thermodynamic data upon the C–F bond cleavage of anion radical species generated during the photocatalysis. Additionally, keto/hemiketal equilibrium was investigated by <sup>19</sup>F NMR spectroscopy to elucidate the ratio of a keto form in ethanol, which is regarded as an active form on the photocatalytic reduction.

## 2. Experimental

### 2.1. Materials

Polycrystalline TiO<sub>2</sub> powder (Degussa P25, specific surface area: 50 m<sup>2</sup> g<sup>-1</sup>) was purchased from Japan Aerosil and used as received. HPLC grade ethanol used for a solvent was purchased from Nacalai Tesque without further purification. The following organic reagents were used as received: AP (Nacalai Tesque, >98.5%), MFAP (Alfa,

>99%), DFAP (SynQuest, >97%), TFAP (Sigma–Aldrich, 99%), AP-OH (TCl, >98%), TFAP-OH (Sigma–Aldrich, 98%).

DFAP-OH was synthesized by the TiO<sub>2</sub> photocatalyzed hydrogenation of DFAP in ethanol as follows: a suspended solution containing DFAP (158 mg, 3 mmol) and P25 TiO<sub>2</sub> (0.1 g) in ethanol (30 mL) was placed in a cylindrical glass cell (40 mm × 45 mm i.d.) and sealed with a rubber septum. To the suspended solution was passed a pure argon gas through the rubber septum for 30 min in the dark, and then irradiated with UV light from a 300 W xenon arc lamp (ILC Technology, CERMAX LX300) through a water filter and cut-off filters (Toshiba UV35) at 32 °C for 12 h. After the irradiation (conversion 83%), the suspended solution was centrifuged to remove the TiO<sub>2</sub> powders, and then evaporated ethanol under reduced pressure to provide a pale yellow residue. Purification was carried out by preparative thin-layer chromatography (SiO<sub>2</sub>, chloroform) to yield 10.4 mg of DFAP-OH as colorless oil (24% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.44 (1H, br, OH), 4.83 (1H, td,  $J_{\text{HF}} = 10.2$  Hz,  $J_{\text{HH}} = 4.7$  Hz, CH), 5.77 (1H, dt,  $J_{\text{HF}} = 55.6$  Hz,  $J_{\text{HH}} = 4.7$  Hz, CF<sub>2</sub>H), 7.26–7.42 (5H, m, C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  73.6 (t,  $J = 24$  Hz, CH), 115.8 (t,  $J = 246$  Hz, CF<sub>2</sub>), 127.1, 128.7, 129.0, 135.8 (t,  $J = 3.5$  Hz, C<sub>Ar</sub>-CH). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta = -127.7$  (1F, ddd,  $J_{\text{FF}} = 284$  Hz,  $J_{\text{FH}} = 56$  Hz,  $J_{\text{HH}} = 9$  Hz),  $-128.3$  (1F, ddd,  $J_{\text{FF}} = 284$  Hz,  $J_{\text{FH}} = 57$  Hz,  $J_{\text{HH}} = 11$  Hz). MS (EI):  $m/z$  (relative intensity) = 158 (M<sup>+</sup>, 15%), 107 (100%), 79 (95%), 77 (63%), 51 (26%). The data are consistent with the previous reports [29,30].

### 2.2. Prolonged UV irradiation experiment

Irradiation experiments were carried out for a mixture of the AP derivatives (initial concentration range: 1–20 mmol L<sup>-1</sup>) and TiO<sub>2</sub> (0.10 g) in deaerated ethanol solution (30 mL) under the irradiation with UV light (>340 nm, light intensity: 790 mW cm<sup>-2</sup>) at 32 °C. The details of irradiation experiment and GC analysis have been described in our previous reports [17–19].

### 2.3. Pre-UV irradiation experiment

The details of this method have been described in our previous reports [18,19]. TiO<sub>2</sub> (0.10 g) in ethanol (30 mL) was placed in the cylindrical glass cell (40 mm × 45 mm i.d.) and sealed with the rubber septum. Argon gas was passed into the suspended solution through the rubber septum for 30 min. The degassed solution was stirred in a water bath for 30 min to attain thermal equilibrium at 32 °C in the dark. During the degassed solution was irradiated with UV light (>340 nm, light intensity: 1250 mW cm<sup>-2</sup>) for 2 h, the white color of TiO<sub>2</sub> powder changed into blue–gray one. After confirming the sufficient color change, 300  $\mu$ mol of the AP derivatives was injected into this TiO<sub>2</sub> suspended solution in the dark. Then, electron transfer from the Ti<sub>3d</sub> sites to adsorbed AP derivatives took place and afforded reductive products. The amount of the products was quantitatively analyzed by GC–MS [18,19].

## 3. Results and discussion

### 3.1. Hemiketal formation in ethanol

The photocatalytic hydrogenation of AP derivatives in ethanol will be influenced by the ketal or hemiketal formation, because the adsorptivity and reactivity on the TiO<sub>2</sub> surface are greatly affected by a concentration ratio of keto/hemiketal/ketal as reported for TFAP [18]. Therefore, keto/hemiketal/ketal equilibrium for MFAP and DFAP was firstly investigated by means of UV absorption and <sup>19</sup>F NMR spectroscopy. Fig. 2 shows UV absorption spectra of MFAP in ethanol (Fig. 2(a)) and DFAP in the mixed solvent of ethanol/CH<sub>3</sub>CN (19/1) (Fig. 2(b)). The absorption spectrum of MFAP with maximum wavelength at 243 and 280 nm did not change with

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