TiO$_2$-photocatalyzed oxidation of adamantane in solutions containing oxygen or hydrogen peroxide

Teruhisa Ohno*, Takahiro Mitsui, Michio Matsumura

Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

Abstract

Photocatalyzed oxidation of adamantane has been investigated using several kinds of TiO$_2$ powders in a mixed solvent of acetonitrile and butyronitrile under aerated conditions. 1-Adamantanol, 2-adamantanol, and 2-adamantanone are obtained as the main products, in which 1-adamantanol is produced at the highest yield. The quantum efficiencies for the production of 1-adamantanol, 2-adamantanol, and 2-adamantanone reach 6.4, 1.0 and 2.1%, respectively. Generally, anatase powders show higher activity than rutile powders. However, by addition of hydrogen peroxide to the solution, the activity of rutile powders is remarkably enhanced and becomes much higher than that of anatase powders. The rate for the production of 1-adamantanol is increased by more than 10 times, and the quantum efficiency for the production of 1-adamantanol reached as high as 25%.
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1. Introduction

A wide range of oxygen-containing molecules including alcohols, aldehydes, ketones, epoxides and carboxylic acids are manufactured by chemical plants and utilized as the starting materials for producing, in particular, plastics and synthetic fiber materials. For producing the oxygen-containing materials, such as carboxylic acids like adipic acid, nicotinic acid, and pyromellitic acid [1,2], nitric acid have been widely used as a useful oxidizing agent. Nowadays, however, demands for replacing the oxidation methods to cleaner ones are increasing, and aerobic oxidations of alkanes leading to alcohol and carbonyl compounds are becoming important processes.

Transformation of adamantane to hydroxylated adamantanes is important because they can be intermediates for the production of photo-resists [3]. However, the reaction conditions are often harsh, and the reaction is non-selective because strong oxidants are required for the oxidation of adamantane [4], which is one of the most stable compounds. For this reason, improvement of the transformation of adamantane to hydroxylated derivatives constitutes an important research area.

Oxidation of adamantane by molecular oxygen has been investigated using some metal complexes or polyoximetalate as the molecular catalysts [5,6]. These catalysts are, however, deactivated with time during reactions [5,6]. In addition, since they are homogeneous catalysts, the isolation of the products is problematic.

Utilization of semiconductor photocatalysts for organic syntheses is attractive because they have strong oxidation power and drive variety of reactions. In addition, these photocatalysts are non-toxic and the reactions are environmentally friendly. By utilizing the strong oxidation power of these semiconductor photocatalysts, many harmful organic compounds included in water and air are successfully mineralized [7–9]. Apart from these mineralization processes, under some experimental conditions, organic compounds are partially oxidized to form diazo compounds [10], epoxides [18,19,23], and aldehydes [22], indicating that photocatalysts can be used for different kinds of organic syntheses [10–23]. In TiO$_2$-photocatalyzed reactions, molecular oxygen can be used as the oxygen source for the partial oxidation of aromatic [24–26] and aliphatic [27,28] compounds. In some cases, water can be used as the oxygen source [29]. These oxygen sources are very attractive from both ecological and economical viewpoints. However, in order to explore the possibility of their application to organic syntheses in practical uses, the efficiency should be further increased. In order to improve the reactions, it is necessary to deepen the

* Corresponding author. Tel.: +81-6-850-6696; fax: +81-6-850-6699.
E-mail address: tohno@chem.es.osaka-u.ac.jp (T. Ohno).

understanding of the photocatalytic reactions because the details remain to be elucidated.

In the present study, we have investigated TiO_2-photo-catalyzed oxidation of adamantane, which is one of the most difficult compounds to partially oxidize by the conventional chemical oxidation processes. We used molecular oxygen or hydrogen peroxide as the oxidants (or sources of oxygen), and different kinds of TiO_2 powders as the photocatalysts.

2. Experimental

2.1. Materials and instruments

Various kinds of titanium dioxide (TiO_2) powders having anatase and/or rutile crystal structures were obtained from Catalysis Society of Japan (TIO-5), Ishihara Sangyo (ST-01, ST-21, ST-41, and PT-101), Toho Titanium (NS-51), and Japan Aerosil (P-25). The content of anatase and the surface area of these powders were as follows: ST-01: 100%, 192.5 m^2/g; ST-21: 100%, 56.1 m^2/g; ST-41: 100%, 8.2 m^2/g; PT-101: 0%, 25.0 m^2/g; NS-51: 1.5%, 6.5 m^2/g; TIO-5: 9%, 2.5 m^2/g; P-25: 73.5%, 49.2 m^2/g. Content of anatase in TiO_2 powders were calculated as follows [30]:

$$\text{Content of anatase (\%)} = \left\{ \frac{I_A}{I_A + 1.265 I_R} \right\} \times 100$$

where I_A and I_R are peak intensities of anatase and rutile, obtained from XRD patterns, respectively. Adamantane, 1-adamantanol, 2-adamantanol, and 2-adamantanone were obtained from Wako Pure Chemical Industry. 1,3-Adamantanediol and 1-hydroxy-4-adamantanone were obtained from Tokyo Chemical Industry Co., Ltd. Other chemicals were obtained from commercial sources as guaranteed reagents and used without further purification. The crystal structures of TiO_2 powders were determined from X-ray diffraction (XRD) patterns measured with a Philips, X'Pert-MRD XRD meter. The surface area of the powders was determined using a surface area analyzer (Micromeritics, FlowSorb II 2300).

2.2. Photocatalytic oxidation of adamantane on photoirradiated TiO$_2$ powders

The mixture of butyronitrile and acetonitrile was used as the solvent for the reaction because of the low solubility of adamantane in acetonitrile. We have confirmed that butyronitrile and acetonitrile are fairly stable under photocatalytic conditions. Photocatalytic reactions were typically carried out in Pyrex glass tubes, to which a mixture of acetonitrile (1.8–2.0 g), butyronitrile (1.96 g), adamantane (40 mg), and TiO_2 powder (0.15 g) was added. The solution was bubbled with oxygen at a rate of 2.0 ml/min for 15 min, and the glass tube was sealed by a septum. During the reaction, the solution was magnetically stirred and externally photoirradiated. A 500 W high pressure Hg-lamp was used as

a light source, and a UV35-filter was employed to remove deep UV light ($\lambda < 350$ nm). Fine stainless meshes were used as neutral density filters to adjust the irradiation intensity. After photoirradiation for certain time periods, the solution was analyzed with a capillary gas chromatograph (Shimadzu GC-14B), equipped with a DB-1 capillary column. The molecular weights of the compounds were determined with a GC–MS spectrometer (JEOL JMS-DX303HF), equipped with a DB-1 capillary column.

The quantum yield of the reaction was determined at a wavelength of 365 nm, which was selected from the Hg-lamp using a band-pass filter (BP-365, Kenko Co.) and a UV-35 filter. The number of irradiated photons was determined from the incident light power measured with a thermopile (Eppley Laboratory); the photon flux was about 4.4×10^{15} s^{-1}. The quantum efficiency was calculated on the assumption that all the irradiated photons were absorbed by TiO_2 particles.

2.3. Photochemical reactions of adamantane in the presence of hydrogen peroxide

In order to clarify the contribution of free OH radicals to the partial oxidation of adamantane, we carried out photochemical reaction of adamantane in the mixed solution of acetonitrile and butyronitrile to which hydrogen peroxide was added, but TiO_2 was not added. In these experiments, the solution in the Pyrex tube was irradiated with the Hg-lamp without using the glass filter (UV-35). By UV irradiation, hydrogen peroxide is photocleaved to OH radicals [31]. The other experimental conditions and analytical methods were the same as those for the TiO_2-photocatalyzed reactions.

3. Results and discussion

3.1. Photocatalytic oxidation of adamantane on the photoirradiation of TiO$_2$

Fig. 1 shows the time course of the photocatalytic reaction, where ST-41 (anatase) was used as the photocatalyst. Production of 1-adamantanol, 2-adamantanol, 2-adamantanone, 1,3-adamantanediol, and 1-hydroxy-4-adamantanone indicates that the TiO_2 powder under irradiation has enough power to oxidize adamantane. Oxidation of adamantane never proceeded in the dark or under irradiation in the absence of TiO_2. The total yield of 1-adamantanol, 2-adamantanol, and 2-adamantanone obtained after photoirradiation for 12 h is about 70% of the amount of adamantane consumed.

When 2-adamantanol was used as a starting material, it was easily oxidized to form 2-adamantanone on the photoirradiation of TiO_2. Hence, it is concluded that 2-adamantanone in the result of Fig. 1 is produced via 2-adamantanol. This is consistent with the result that the amount of 2-adamantanol levels off as increase of the
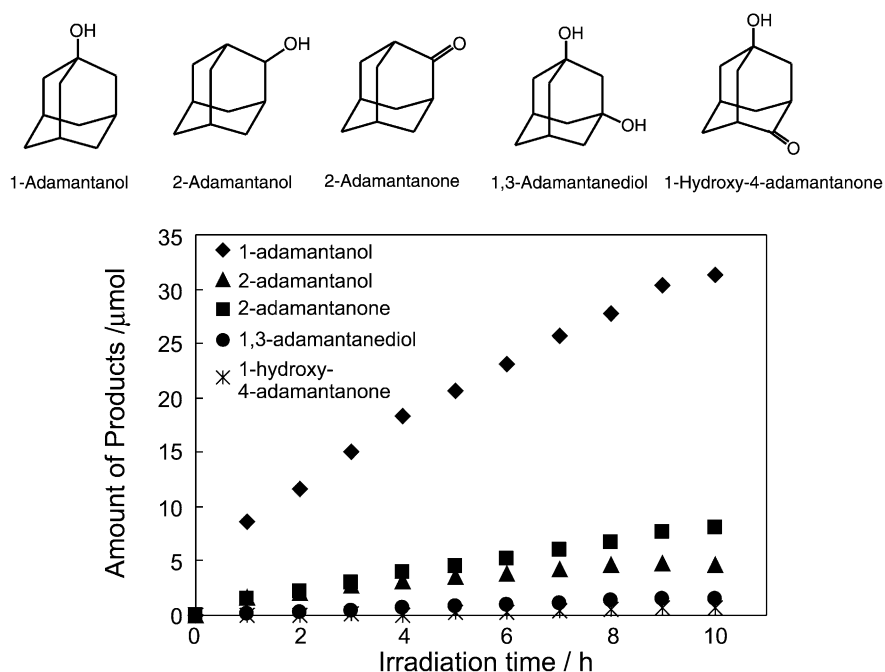
Fig. 1. Time courses for the TiO$_2$-photocatalyzed production of 1-adamantanol, 2-adamantanone, 2-adamantanol, 2-adamantanone, 1,3-adamantanediol, and 1-hydroxy-4-adamantanone from adamantane. The reaction was carried out in a mixed solvent of CH$_3$CN (2.0 g) and C$_3$H$_7$CN (1.96 g) containing adamantane (40 mg) and TiO$_2$ powder (ST-41, 100 mg) as the photocatalyst. The light beam was passed through a glass filter (UV-35) to remove deep UV light ($\lambda < 340$ nm). The detailed experimental conditions are described in Section 2.

amount of 2-adamantanone during photoirradiation. It should be noted that the 1-adamantanol is produced at a fairly high rate for the initial 1 h after starting photoirradiation, and the rate is decelerated as the irradiation continues, as shown in Fig. 1. This is probably because the reaction rate of adamantane is lowered by the preferential oxidation of the reaction products, especially 2-adamantanol, on the surface of photoirradiated TiO$_2$.

Concerning dihydroxylated compounds, we only obtained 1,3-adamantanediol. Production of 1,4-adamantanediol is suggested because we obtained 1-hydroxy-4-adamantanone, which is probably generated by oxidation of 1,4-adamantanediol. Structurally, there are five possible adamantanediols. However, we did not obtain 1,2-adamantanediol, 2,4-adamantanediol, 2,6-adamantanediol, or their further oxidized products. This result suggests that the further oxidation or ring opening reactions of these adamantanediols proceed rapidly.

Photocatalytic activity of various kinds of TiO$_2$ powders were investigated and the results obtained using some of the powders are shown in Fig. 2. In all the cases, 1-adamantanol, 2-adamantanol, and 2-adamantanone were the main products. Among the TiO$_2$ powders we investigated, the ST-41 powder shows the highest activity. Generally, anatase powders show a little higher activity than rutile powders, although the dependence of the activity on the crystal structure and the particle size is small. This is in contrast to the fact that in many photocatalytic reactions of organic compounds, TiO$_2$ powders consisting of small anatase particles, such as

ST-01, show high activity [32]. This is probably because the concentration of adamantane under our experimental conditions is rather high; the small TiO$_2$ particles are suited to the reactions where the concentrations of reactants are low.

The quantum efficiencies for the production of 1-adamantanol, 2-adamantanol, and 2-adamantanone using the ST-41 powder were 6.4, 1.0 and 2.1%, respectively, which were determined after irradiation at 365 nm for 1 h. The quantum efficiencies were calculated on the assumption that two photons are used for producing one 1-adamantanol or 2-adamantanol molecule, and four photons are used for production of one 2-adamantanone. These quantum efficiencies are lower than those for the oxidation of alcohols, which are oxidized at the quantum efficiency of about 100% under similar experimental conditions [33]. This result suggests that the oxidation of adamantane is difficult even using photoirradiated TiO$_2$, probably because of its chemical robustness. However, we found that the efficiency can be enhanced by addition of hydrogen peroxide as discussed later.

3.2. Oxidation of adamantane by OH radicals

In order to determine whether or not free OH radicals are involved in the reaction, we carried out the photochemical reaction of adamantane in a mixture of acetonitrile and butyronitrile containing hydrogen peroxide without the addition of TiO$_2$ powder. For this reaction, light with wavelengths longer than 300 nm was irradiated, and OH radicals were provided to the solution as the result of the
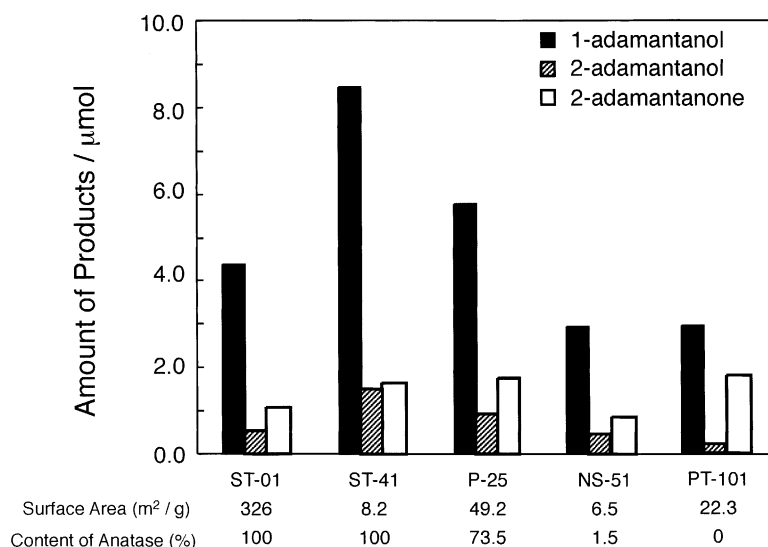
Fig. 2. Amounts of 2-adamantanone, 2-adamantanol, and 2-adamantanone produced from adamantane after photoirradiation for 1 h using several TiO_2 powders. Physical properties of the powders are shown beneath the graph. Experimental conditions are the same as those of Fig. 1.

dissociation of O–O bonds of hydrogen peroxide [31]. While the photoirradiation continued, adamantane was oxidized, and products similar to those of the TiO_2-photocatalyzed reaction were obtained, as shown in Fig. 3(b). Fig. 3(a) shows the results obtained by the TiO_2-photocatalyzed reaction, to which a small amount of water was added in place of 35% hydrogen peroxide. By comparing the results, we find that the distribution of the products of the photochemical reaction is quite different from that of the TiO_2-photocatalyzed reaction. More precisely, 1-adamantanol was obtained at the highest yield for the TiO_2-photocatalyzed reaction,

while 2-adamantanol was obtained at the highest yield for the photochemical reaction. In other words, hydroxylation occurs preferentially at the tertiary carbons in the TiO_2-photocatalyzed reaction, and at the secondary carbons in the photochemical reaction. It is worth noting that there is no effect of water on the reaction rate and distribution of the products on TiO_2 photocatalytic reactions if one compares the results, for example, of ST-41 in non-aqueous solution (Fig. 2) with the one in the presence of a small amount of water (Fig. 3(a)).

In the case of the photochemical reaction in the presence of hydrogen peroxide, free OH radicals are considered to randomly subtract H atoms from adamantane, which has 12 H atoms at the secondary carbons and four H atoms at the tertiary carbons (the ratio is 3). The adamantane radicals generated as a result of the H-atom subtraction are expected to react with OH radicals to form hydroxylated adamantanes. Hence, the amount of hydroxylated adamantane at the secondary carbons is expected to be about three times as large as that of hydroxylated adamantane at the tertiary carbons. This is in accordance with the result of Fig. 3(a) which shows that the total amount of 2-adamantanol and 2-adamantanone is about three times of the amount of 1-adamantanol. Therefore, the fact that the distribution of the products of the TiO_2-photocatalyzed reaction is different from that of the photochemical reaction suggests that the active species in the former reaction is not free OH radicals, as will be discussed later in more detail.
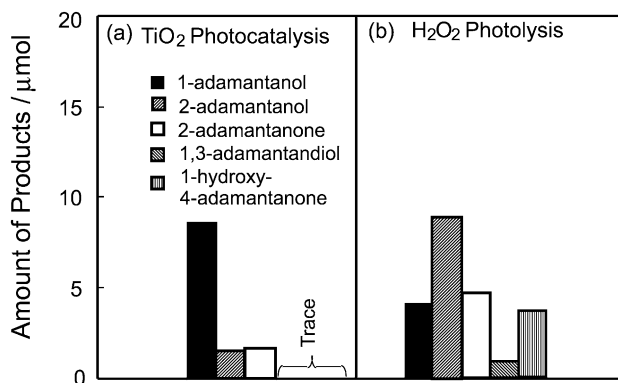

Fig. 3. Amounts of 2-adamantanone, 2-adamantanol, 2-adamantanone, 1,3-adamantanediol, and 1-hydroxy-4-adamantanone produced from adamantane by the TiO_2-photocatalyzed reaction (a) and by the photochemical reaction with hydrogen peroxide (b). There reactions were carried out for 1 h. Experimental conditions of the TiO_2-photocatalyzed reaction (a) were the same as those of Fig. 1, except that, in this experiment, water (100 mg) was added to the solution. The photochemical reaction (b) was carried out in the solution to which 30% hydrogen peroxide (100 mg) instead of water is added without addition of TiO_2 powder, and the solution was directly irradiated without using the glass filter (UV-35), which was used for the TiO_2-photocatalyzed reaction.

3.3. TiO_2-photocatalyzed oxidation of adamantane in the presence of hydrogen peroxide in solution

When hydrogen peroxide was added to the solution of the TiO_2-catalyzed reaction, oxidation of adamantane was
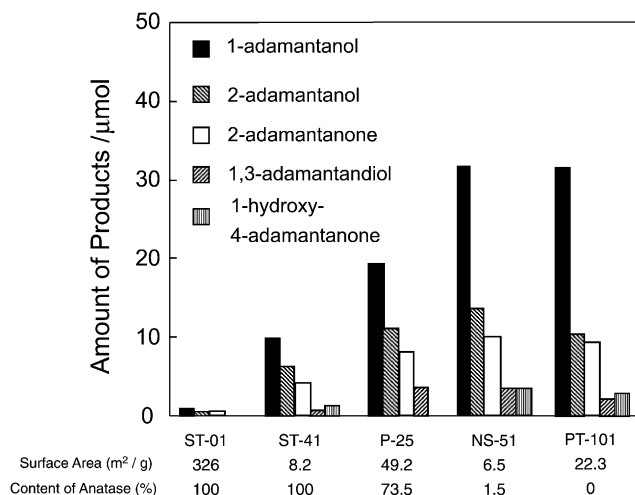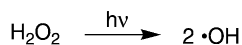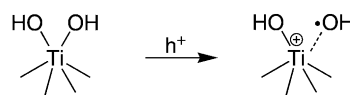
Fig. 4. Amounts of 2-adamantanone, 2-adamantanol, 2-adamantanone, 1,3-adamantanediol, and 1-hydroxy-4-adamantanone produced from adamantane after photoirradiation for 1 h using several TiO$_2$ powders in the solution containing hydrogen peroxide. Experimental conditions are the same as those of Fig. 1, except that, in this experiment, 30% hydrogen peroxide (100 mg) was added to the solution.

Scheme 2. Generation of OH radical on the surface of photoirradiated TiO$_2$.
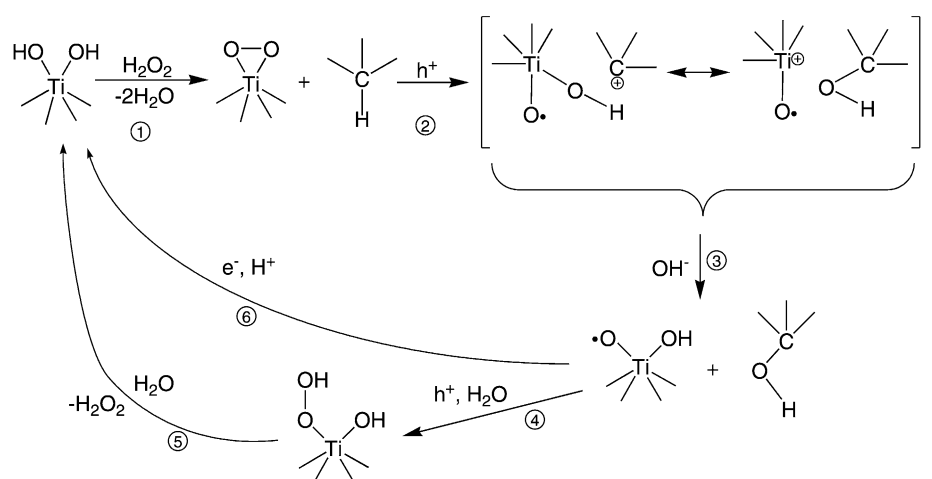
3.4. Proposed mechanism for the TiO$_2$-photocatalyzed oxidation of adamantane

As discussed above, when adamantane is oxidized by photochemical reaction with free OH radicals produced by H$_2$O$_2$ (Scheme 1), the main products are 2-adamantanol and 2-adamantanone. This is because free OH radicals randomly subtract H atoms from adamantane, and the number of H atoms bonded to the secondary carbon atoms of adamantane is higher than the H atoms bonded to the tertiary carbon atoms. On the other hand, when adamantane is oxidized on photoirradiated TiO$_2$ particles using molecular oxygen or hydrogen peroxide as the electron acceptor, the main product is 1-adamantanol. This result suggests that the active species involved in this reaction is not free OH radicals.

For the reactions using molecular oxygen as the electron acceptor, we assume that the active species are OH radicals generated on the surface of TiO$_2$ (Scheme 2), which may be the same as surface trapped holes [36]. In Scheme 2, h$^+$ stands for a positive hole photogenerated in TiO$_2$. Because of the long life and lowered activity of these species generated on the surface of TiO$_2$, the reaction occurs via the most stable intermediate, i.e., adamantane radical at the tertiary carbons.

As for the effect of hydrogen peroxide on the TiO$_2$-photocatalyzed reaction, an important result is that only rutile powders show drastic enhancement of the activity. In the presence of hydrogen peroxide, electrons are donated from TiO$_2$ to hydrogen peroxide because it is a stronger oxidant than molecular oxygen. When hydrogen peroxide accepts an electron, OH radical may be produced [37]. If OH radicals are generated in large amounts, they can enhance the reaction with adamantane. However, we do not consider this process as the reason for the enhanced activity, because this reaction could have occurred for both on rutile and anatase particles, but the enhancement is observed only for rutile particles.

An important point is why the enhanced activity by the addition of hydrogen peroxide is observed only for rutile particles. Hydrogen peroxide forms complexes on the surface of TiO$_2$ particles, and both rutile and anatase powders changes into yellow. By measuring FTIR spectra, we found that Ti-η^2 peroxide complex is generated on the surface of rutile TiO$_2$ [23]. On the other hand, mainly Ti-μ^2 peroxide is generated on the surface of anatase TiO$_2$ [23]. On the basis of these results, although the details remain to be clarified, we propose Scheme 3 for the oxidation of adamantane on photoirradiated rutile TiO$_2$ particles. Probably because the active species photogenerated on the surface of TiO$_2$ (Step 2 in Scheme 3) is less active than free OH radicals,

significantly increased if rutile TiO$_2$ powders were used as the photocatalysts, as shown in Fig. 4. The PT-101 and NS-51 powders, which chiefly consist of rutile particles, show large enhancement, and the observed activity was more than 10 times higher than the activity obtained in the absence of hydrogen peroxide (compare Figs. 2 and 4). It should be noted that the fraction of 2-adamantanol in the products is increased by the addition of hydrogen peroxide. This result suggests that the photochemical reaction contributes to the enhancement of the photocatalytic reaction to some extent. However, the large enhancement in the production of 1-adamantanol by the addition of hydrogen peroxide cannot be explained by this effect.

In contrast to the cases of rutile TiO$_2$ powders, practically no enhancement was observed for most of anatase TiO$_2$ powders. Furthermore, when the particles were very small, the activity was even lowered by the addition of hydrogen peroxide, as shown in Fig. 4 for the case of the ST-01 powder. This is probably due to the formation of surface complex with hydrogen peroxide [34]. The amount of complex formed on these small particles is large because of its extremely large surface area. As a result, the photoexcitation of TiO$_2$ is hindered because a large part of the irradiated UV light is absorbed by the surface complex. In the case of P-25, which is a mixture of 30% rutile and 70% anatase particles [35], the effect of the hydrogen peroxide addition is between those for rutile and anatase powders, and the production of 1-adamantanol was enhanced by 2.6 times.

Scheme 1. Generation of free OH radicals by photocleavage of hydrogen peroxide.

Scheme 3. Proposed mechanism for the enhanced hydroxylation of adamantane on the surface of photoirradiated rutile TiO_2 particles by the addition of hydrogen peroxide.

oxidation of adamantane occurs chiefly on the ternary carbons. In Step 5, we assume that hydrogen peroxide is reproduced. In practice, however, we have to add a large amount of hydrogen peroxide to continue the reaction at high efficiency. This is because hydrogen peroxide is decomposed through many processes, such as reduction and oxidation on the TiO_2 surface. In the case of anatase particles, the Ti-μ^2 peroxide complex is considered to be inactive for oxidation of adamantane, as it is inactive for the oxidation of olefins and naphthalene [21].

4. Conclusion

Although adamantane is one of the most stable organic compounds, we found that it can be oxidized into 1-adamantanol, 2-adamantanol, and 2-adamantanone using TiO_2 photocatalysts. It is also found that the efficiency is greatly improved by addition of hydrogen peroxide to the reaction solution, if rutile TiO_2 is used as the photocatalyst. The reaction is interesting from a viewpoint of organic syntheses, especially, in connection with green chemistry, because the stable compound can be converted to the hydroxylated derivatives using molecular oxygen or hydrogen peroxide as the oxygen sources by utilizing photon energy.

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