

Epoxidation of Olefins on Photoirradiated Titanium Dioxide Powder Using Molecular Oxygen as an Oxidant

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Linear alkyl olefins were oxidized to epoxides on photoirradiated TiO₂ powder by molecular oxygen. The reaction rate was significantly dependent on the kind of TiO₂ powders used as the photocatalyst. Using an active TiO₂ powder, 1,2-epoxyhexane was obtained with a yield of 79% of 1-hexene consumed. The highest epoxidation velocity was obtained for 1-decene. The quantum efficiency of this reaction was 2.2%. Both the yields and the efficiencies of the epoxidation of the linear olefins were much higher than those reported for arylated olefins. © 1998 Academic Press

INTRODUCTION

Many studies have been carried out on epoxidation of olefin compounds (1–8) because epoxides are important starting materials for the synthesis of polymers. In laboratories, epoxides are synthesized by partial oxidation of olefins using iodossylbenzene, hypochlorite, or organic hydroperoxides as the oxidants. For these reactions, porphyrin compounds are often used as the catalysts (9–12). Peracetic acid is also known as an efficient oxidant for the epoxidation of olefins (13).

Molecular oxygen, which is the most attractive oxidant from the economical and environmental viewpoint, has also been reported to be an oxidant for the synthesis of epoxides using some porphyrin compounds as the catalysts (14, 15). The catalysts are, however, deactivated if the reactions are continued for a long period. For example, Ru-porphyrin loses the catalytic activity as the result of coordination of carbon monoxide to the nuclear ruthenium (IV) atom. In the case of Nb-porphyrin, which has the catalytic effect under photoirradiation, it is gradually photodecomposed. Another disadvantage of these reactions is that isolation of products is problematic from the reaction mixture in a homogeneous phase.

In contrast to the above molecular catalysts, semiconductor photocatalysts have advantages in their stability and separability from the reaction mixture. Because of these advantages, they have been studied in the fields

of organic syntheses (16–19) and treatments of wastes (20–22). For epoxidation of olefins, Kanno *et al.* (23) reported that 1,1-diphenylpropylene was oxidized to 1,1-diphenylepoxypropane by photoirradiation of TiO₂ or CdS particles suspended in oxygenated solutions. However, in their results the main product was not epoxide but ketone. Fox *et al.* (24, 25) also reported that arylated olefins were oxidized on photoirradiated semiconductor particles in air-saturated acetonitrile solutions to yield small amounts of epoxides, carbonyl compounds being the main products in most cases (24, 25). Although the yields in their reports are low, the generation of epoxides on photocatalysts using molecular oxygen as the oxidant is noteworthy. In this paper, we report that efficient photocatalytic epoxidation is attained using linear olefins as the substrates and some kinds of TiO₂ powders as the photocatalysts.

EXPERIMENTAL

Materials

Various kinds of titanium dioxide (TiO₂) powders having anatase and rutile forms were obtained from the Catalysis Society of Japan (JRC-TIO-2, -3, and -5), Ishihara Sangyo Ltd. (ST-01), Japan Aerosil (P-25), and other sources. The crystal structures and the surface area of some of the representative powders were as follows: JRC-TIO-2, anatase, 14.6 m²/g; JRC-TIO-3, rutile, 42.5 m²/g; JRC-TIO-5, rutile, 2.2 m²/g; P-25, anatase (70%), 44.4 m²/g; ST-01, anatase, 192.5 m²/g. 1-decene, 2-decanone, nonanal, tetrabutylammonium perchlorate (TBAP), and acetonitrile were purchased from Wako Pure Chemical Industries. 1-hexene, 1-hexadecene, 1,2-epoxyhexane, 1,2-epoxydecane, 1,2-epoxyhexadecane, pentanal, 2,6-di-tert-butyl-p-cresol, n-hexane, nitromethane, and n-butyronitrile were purchased from Tokyo Kasei. They were all guaranteed-grade reagents and used without further purification.

Photocatalytic Oxidation of Olefins on TiO₂ Powder

Photocatalytic reactions were carried out in a Pyrex glass tube (ϕ 10 mm), which contained TiO₂ powder (15 mg) and

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an olefin compound (4.0 g). Some experiments were carried out in solutions of acetonitrile, n-hexane, nitromethane, and n-butyronitrile. During the photocatalytic reactions, oxygen gas was passed through the liquids at a flow rate of 3.0 ml/min, and the TiO_2 particles were suspended in the liquids with a magnetic stirrer. The suspensions were photoirradiated with a 500-W high-pressure Hg lamp (Wacom R&D, BMO-500DI) at room temperature. The light beam was passed through a Pyrex glass filter, to cut off wavelengths shorter than 300 nm, and a fine stainless mesh, to adjust the irradiation intensity. The total intensity of light incident on the reaction tube was about 40 mW. Products generated by photocatalytic reactions were analyzed by gas-liquid chromatography (JEOL JGC-20 K) using a Shimadzu C-R6A-FFC chromatopac for data processing. The reaction products were identified by coinjecting corresponding authentic samples. The injection temperature (Ti), column temperature (Tc), and detector temperature (Td) of GLC for some starting materials were as follows; 1-hexene (Ti, 110°C; Tc, 80°C; Td, 110°C), 1-decene (Ti, 200°C; Tc, 220°C; Td, 220°C), 1-hexadecene (Ti, 240°C; Tc, 220°C; Td, 240°C). The retention times of some typical compounds under the above conditions were 0.8 min (1-hexene), 4.3 min (1,2-epoxyhexane), 0.9 min (1-decene), 2.2 min (1,2-epoxydecane), 5.2 min (1-hexadecene), and 13.3 min (1,2-epoxyhexane).

For determination of the quantum efficiency of photocatalytic reactions, the suspensions were irradiated with the emission band at wavelengths around 365 nm from the high pressure mercury lamp. The emission band was selected using band-pass glass filters. The number of photons irradiated on the test tubes per second was determined to be about $1.3 \times 10^{16} \text{ s}^{-1}$ using an thermopile (Eppley Laboratory).

Redox Behavior of Olefin Compounds

Cyclic voltammograms of olefins in acetonitrile were obtained using a Nikko-Keisoku potentiostat NPOT-2501 and a Nikko-Keisoku potential sweeper NPS-2A. An Ag/AgCl electrode was served as a reference, which was separated from a bulk electrolyte solution using a salt bridge. The solutions containing the olefin compounds ($5.5 \times 10^{-4} \text{ M}$) and TBAP ($5.0 \times 10^{-2} \text{ M}$) as the supporting electrolyte were deaerated by bubbling with argon gas, prior to each measurement, and maintained under argon atmosphere throughout the measurement.

RESULTS AND DISCUSSION

While TiO_2 particles suspended in olefin compounds were photoirradiated under a stream of oxygen bubbles, the aliquots of the reaction liquid were periodically sampled to analyze the products. Typical results of the photocatalytic reaction are shown in Fig. 1, where 1-decene was

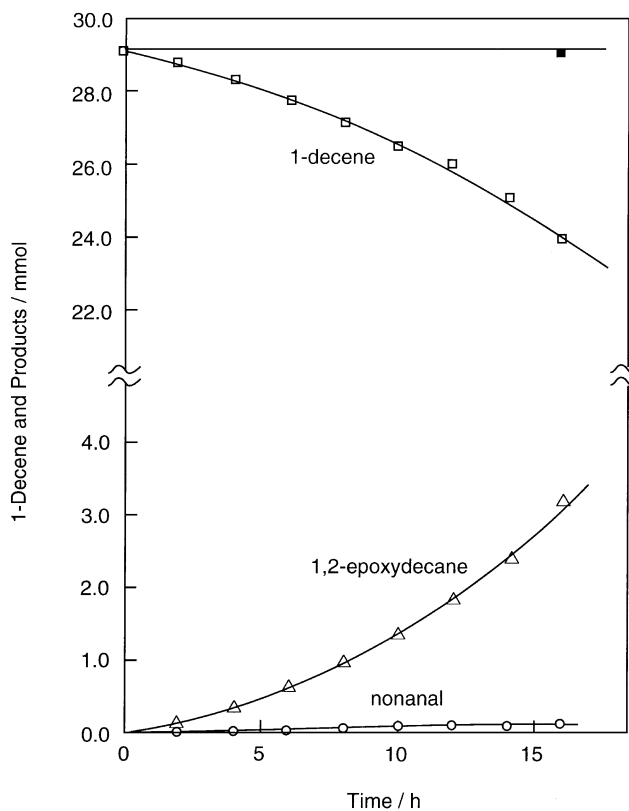


FIG. 1. Change of the amounts of 1-decene, 1,2-epoxydecane, and nonanal in a test tube as the result of photocatalytic reaction. The reaction was carried out in pure 1-decene (4.0 g, 2.9×10^{-2} mol) using TiO_2 powder (ST-01, 15 mg) as the photocatalyst under a stream of oxygen bubbles. The amount of 1-decene after photoirradiation for 16 h under a stream of oxygen bubbles is marked with a closed square.

used as the substrate and TiO_2 (ST-01) was used as the photocatalyst. By photoirradiation, 1,2-epoxydecane increased steadily with the decrease of 1-decene. A small amount of nonanal was also generated in the solution, whose concentration leveled off at the irradiation time of about 10 h. Generation of other compounds was suggested from the difference in the amounts of 1-decene decreased and the 1,2-epoxydecane and nonanal produced. Production of a very small amount of 2-decanone was confirmed by gas-chromatography at a retention time of 2.4 min. Although unidentified, other products with retention times at 4.5, 5.3, and 7.8 min were also detected by gas-chromatography.

When the passing gas of oxygen was replaced with argon, practically no reaction was observed by irradiation of the TiO_2 suspension containing 1-decene, as shown by a closed square in Fig. 1. This result indicates that molecular oxygen is the oxidant for the oxidation of 1-decene to produce the epoxide and other products.

To evaluate the reactivity of the products on the photoirradiated TiO_2 particles, photocatalytic reactions were carried out in acetonitrile solutions of 1,2-epoxydecane

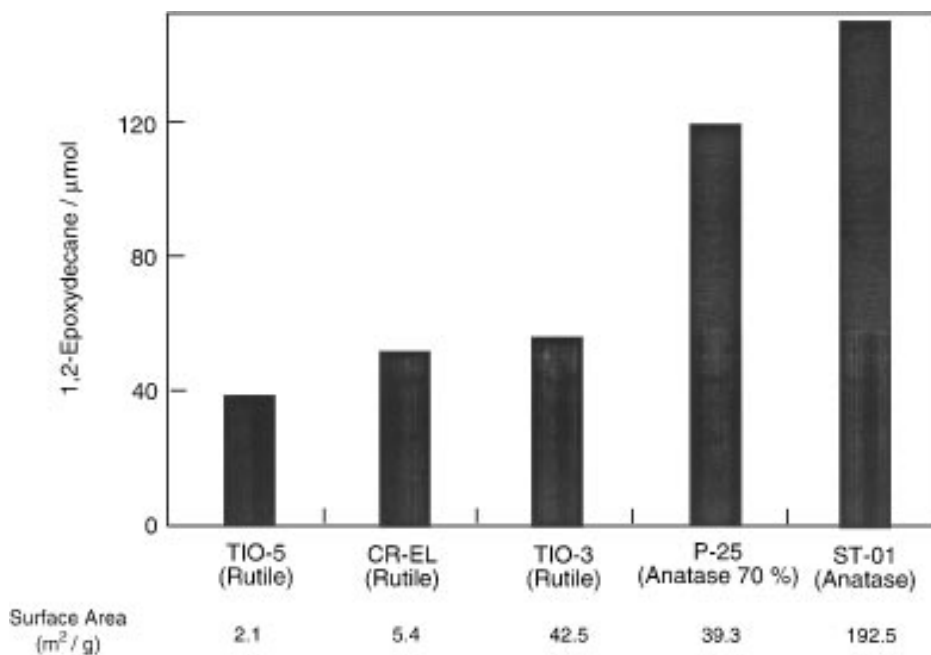


FIG. 2. Comparison of the photocatalytic activities of TiO₂ powders for producing 1,2-epoxydecane from 1-decene. The reactions were performed by photoirradiation for 19 h in acetonitrile solutions of 1-decene (4.0 ml, 0.29 M) containing 15-mg TiO₂ powder under a stream of oxygen bubbles.

(0.45 M) and nonanal (0.45 M) under a stream of oxygen. The amount of 1,2-epoxydecane was practically not changed by photoirradiation for 19 h. On the other hand, nonanal was photocatalytically decomposed very fast. Hence, the small amount of nonanal observed in Fig. 1 during irradiation is considered to arise from the balanced rates of its production and decomposition on the photoirradiated TiO₂ particles. It is also considered that the decomposition of nonanal should be a part of the reason for the generation of unidentified products.

Using any TiO₂ powders as the photocatalyst, 1,2-epoxydecane was always obtained as the main product from 1-decene. However, the reaction rate was strongly dependent on the TiO₂ powders. Among the TiO₂ powders we examined, ST-01 showed the highest reaction rate and P-25 followed it, as shown in Fig. 2. These active TiO₂ powders have the anatase crystalline form. This result suggests that the amount of oxygen adsorbed on TiO₂ is crucial in the reactivity, as it is known that the anatase-form TiO₂ powders have a higher capability to adsorb oxygen than rutile-form powders (26), probably due to their large surface area. A similar relationship between the reactivity and the crystalline form has been reported on various photocatalytic reactions of organic compounds (20–22).

Figure 3 shows the reactivity of some typical olefins on photoirradiated TiO₂ (ST-01). The reaction rate became the highest for the olefins with about 10 carbons. The quantum efficiency of the generation of 1,2-epoxydecane from 1-decene was determined to be 2.2%. In this experiment,

TiO₂ (ST-01) suspended in 1-decene was irradiated with light at around 365 nm for 4 h (see Experimental section for details). In the determination of the quantum efficiency, it was assumed that the light quanta incident on the test tube were all adsorbed by TiO₂ particles and the reflections at glass tube and photocatalysts were ignored. The actual quantum efficiency of the reaction, therefore, is expected to be about 3%.

The ratio of epoxides produced to the olefins consumed (chemical yield) increased with the decrease of the chain length. In the case of 1-hexene, it reached as high as 79%. On the other hand, the ratio became low with the increase of the chain length, as shown in Fig. 3.

It should be emphasized that the production rates and the chemical yields of epoxides were much higher than those reported by Kanno *et al.* (23) and Fox *et al.* (24, 25). The efficient production of epoxides in our study is attributable to the reaction performed in neat olefin liquids and the choice of an efficient TiO₂ photocatalyst. The difference in the reactivity between arylated and nonarylated olefins should be another reason.

When the reactions were carried out in solutions, the reaction rates for the production of epoxides were strongly dependent on the solvents, as shown in Fig. 4 for the reactions of 1-decene. In the measurements, P-25 was used as the photocatalyst. All the reaction rates were lower than that of pure 1-decene by more than one order of magnitude. The dependence of the reaction rate on the kinds of solvents is discussed later.

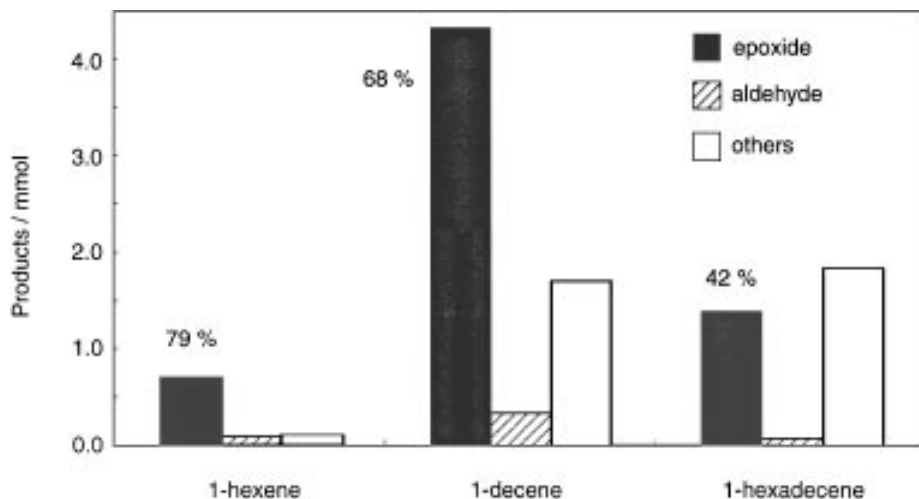


FIG. 3. Amounts of epoxides, aldehydes, and other species produced from pure 1-hexene, 1-decene, and 1-hexadecene ($4.0 \text{ g}, 1.8\text{--}4.8 \times 10^{-2} \text{ mol}$) by photocatalytic reactions on TiO_2 powder (ST-01, 15 mg). Suspensions were photoirradiated for 19 h under a stream of oxygen bubbles. The numbers beside the bars of epoxides stand for the ratios of the amounts of epoxides produced to the amounts of olefins consumed. The total amounts of others were determined from the difference between the amounts of olefins consumed and epoxides and aldehyde produced.

Concerning the mechanism of the photocatalytic oxidation of arylated olefins on semiconductor photocatalysts, Kanno *et al.* (23) and Fox *et al.* (24, 25) proposed that the olefins are initially oxidized by the photogenerated positive holes to form cation radicals. At the same time, oxygen is reduced by the electrons to superoxide ions. The olefin cation radicals react with superoxide ions to produce dioxetane compounds, which are unstable at room temperature and

thermally decompose into the products (27). This mechanism explains the production of aldehydes, which were the main products in most of their experiments. However, this mechanism cannot explain the production of epoxides because epoxides are not generated from dioxetanes (27).

For the production of epoxides, we propose the mechanism shown in Fig. 5. The participation of cation radicals

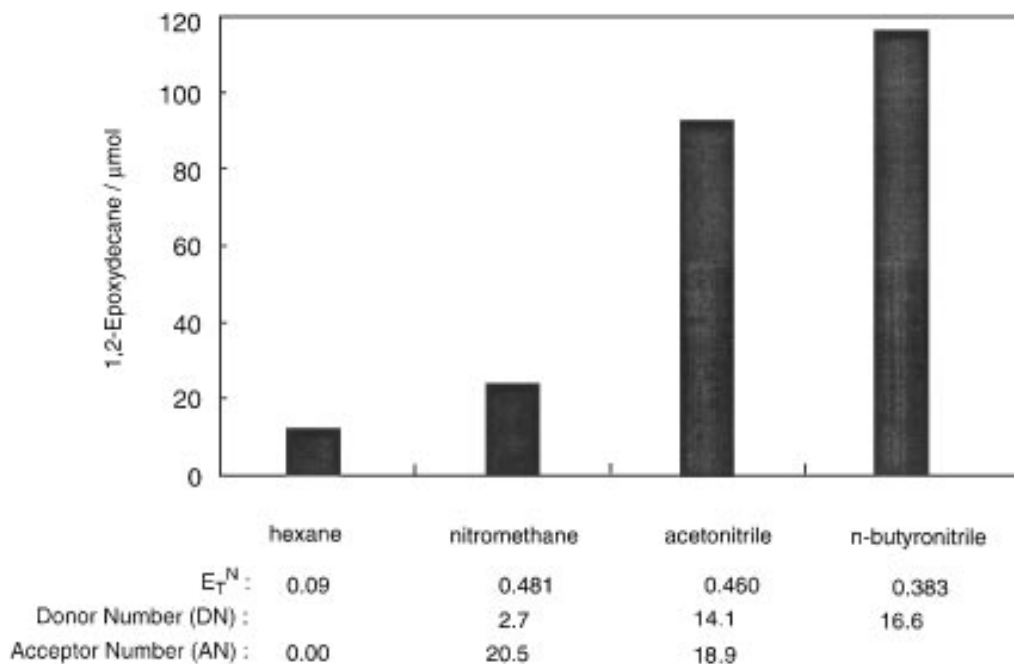


FIG. 4. Amounts of 1,2-epoxydecane produced by photocatalytic reactions on TiO_2 particles (P-25, 15 mg) suspended in hexane, nitromethane, acetonitrile, and butyronitrile. Reactions were carried out for 19 h in solutions (4.0 ml) containing 1-decene ($0.16 \text{ g}, 1.14 \times 10^{-3} \text{ mol}$) under a stream of oxygen bubbles (3.0 ml/min). The E_T^N -values (28), donor numbers (29), and acceptor numbers (30) of the solvents are shown beneath the figure.

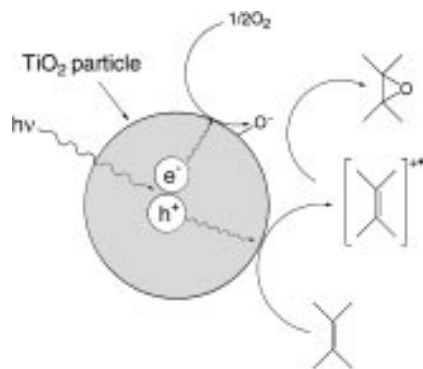


FIG. 5. A possible mechanism for the generation of an epoxide compound from an olefin compound on a photoirradiated TiO_2 particle.

of the olefins in the mechanism is proved by the following experimental results. First, the oxidation potentials of 1-hexene, 1-decene, and 1-hexadecene measured by cyclic voltammogram in acetonitrile were 0.99, 0.98, and 1.0 V versus Ag/AgCl , respectively. Since these oxidation potentials are much lower than the positive holes photo-generated in TiO_2 , the olefins are oxidizable to the cation radicals on TiO_2 . Second, by addition of 2,6-di-tert-butyl-4-methylphenol, which is an efficient scavenger of cation radicals, to the suspension, the production of epoxides and aldehydes is inhibited, as Kanno *et al.* (23) observed the effect for the reactions of arylated olefins.

In addition, the effect of solvents on the reaction rate, as shown in Fig. 4, gives some insight into the reaction mechanism. From the comparison of the reactivity of olefins and the polarity parameters of the solvents, i.e., E_T^N -values (28), donor numbers (DN) (29), and acceptor numbers (AN) (30), the reactivity is found to be strongly correlated with the donor number. As to hexane, although the donor number is not reported, a smaller value than those of the other solvents is expected, because it has very poor nucleophilicity. Since a solvent with a large donor number favors the stabilization of cationic species, the correlation suggests that the formation of the cationic radicals of olefins is the crucial step of the photocatalytic epoxidation of TiO_2 particles.

The question is the source of oxygen for producing epoxides. As discussed previously, the production of epoxides via dioxetanes is unlikely. Thus, oxygen should be supplied from species other than O_2^- ions. Agustin *et al.* observed the generation of O^- species on the photoirradiation of TiO_2 surface under an aerated condition by means of an ESR spectrometer (31). We suppose that this is the source of oxygen because such a mono-oxygen species most likely produces epoxides when they react with the cation radicals of olefins, although there might be other possibilities.

Thermodynamically, positive holes in TiO_2 particles have an oxidation power high enough to oxidize olefins to the cation radicals. However, without oxygen or other electron

acceptors, the rate of this reaction and those of the successive reactions must be negligibly low, because the electrons left in the TiO_2 particles lead to enhanced electron-hole recombination. This is in agreement with the experimental results that practically no products were obtained in the absence of oxygen.

CONCLUSION

We have demonstrated that photocatalytic oxidation of linear olefins to epoxides proceeds at high efficiency on some kinds of TiO_2 powders under photoirradiation using molecular oxygen as the electron acceptor. The TiO_2 powders used in the experiments are quite stable and are easily separated from the reaction solutions. In addition, the reaction rate can be raised by increasing the power of the light source. We, therefore, consider that photocatalytic epoxidation of olefins has a good chance to be applied to practical syntheses of epoxide compounds.

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