Stereospecific Epoxidation of 2-Hexene with Molecular Oxygen on Photoirradiated Titanium Dioxide Powder

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(Received May 27, 1998; CL-980405)

Photocatalytic oxidation of 2-hexene on TiO_2 powder was investigated under a stream of oxygen gas. The main product was 2,3-epoxyhexane with the chemical yield ranging from 65% to 83% depending on the TiO_2 powders. When *trans*-2-hexene was used as the starting material, the epoxide was also *trans*. On the other hand, *cis* epoxide was the chief product from *cis*-2-hexene. From mixed 2-hexene (*trans*/*cis* = 1.7), larger amounts of *trans* epoxide were obtained than *cis*-epoxide in the initial period of the reaction, indicating that *trans*-2-hexene is more reactive than the *cis* isomer on the photocatalyst.

Epoxidation of olefin compounds utilizing molecular oxygen is advantageous from the economical and environmental viewpoint. However, the commercial epoxide synthesized using molecular oxygen is limited to ethylene oxide. Recently, we have found that photocatalytic epoxidation of linear olefins such as 1-hexene, 1-decene, and 1-hexadecene, proceeds on photoirradiated TiO_2 powder at high chemical yield under a stream of oxygen.[1] Before our study, Kanno et al.[2] and Fox et al.[3,4] had reported photocatalytic epoxidation of aromatic olefins. Our observation was in contrast to these previous reports in that the efficiency can be raised much higher. Here, we report that the epoxidation of linear olefins proceeds stereospecifically.

As the starting materials of this work, we used 2-hexene consisting of *trans* and *cis* isomers at a ratio of 1.7 : 1, and *trans*- and *cis*-2-hexene. *trans*-2-Hexene and mixed 2-hexene were purchased from Tokyo Kasei, and *cis*-2-hexene was obtained by distillation of the mixed 2-hexene, followed by gel filtration chromatography on a column of Toyopearl HW-40/Fine using methanol as eluant. Photocatalytic reactions were carried out using various kinds of TiO_2 powders in Pyrex glass tubes (ϕ 10 mm), which contained TiO_2 powder (20 mg) and 2-hexene (2.0 g, 2.4 x 10^{-2} mol). The suspension was stirred with a rotating magnetic bar and bubbled with a oxygen stream. The reaction tubes were externally photoirradiated using a 500 W high-pressure Hg lamp. The light beam was passed through a Pyrex glass filter and a fine stainless mesh to cut-off wavelengths shorter than 300 nm and to lower irradiation intensity, respectively. The intensity of incident light on the reaction tube was about 40 mW. Products generated by photocatalytic reactions were analyzed by a gas-liquid chromatography (JEOL JGC-20K) with a Shimadzu C-R6A-FFC chromatopac for data processing. The products were identified by coinjection of the corresponding authentic samples into a column of PEG-1000. 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 number of photons irradiated on the test tubes per second was determined to be about 1.3 x 10^{16} s^{-1} using iron oxalate solution as the actinometer.

As the result of the photocatalytic reaction of 2-hexene (*trans*/*cis* = 1.7) under a stream of oxygen, *trans*- and *cis*-2,3-epoxyhexane was generated, as shown in Figure 1. Very small amounts of 1,2-epoxyhexane and n-butylaldehyde were also produced in the solution. Generation of a small amount of 1,2-epoxyhexane is attributed to the photocatalytic isomerization of 2-hexene to 1-hexene on the photo-irradiated TiO_2 powder.[5] Practically no products were obtained if reaction was performed under an argon stream, indicating that molecular oxygen is the source of oxygen of the epoxidation. The reaction rate was accelerated as the reaction continued, suggesting that hydrogen peroxide or superoxide, which was produced by the reduction of oxygen, was involved in the reaction mechanism.

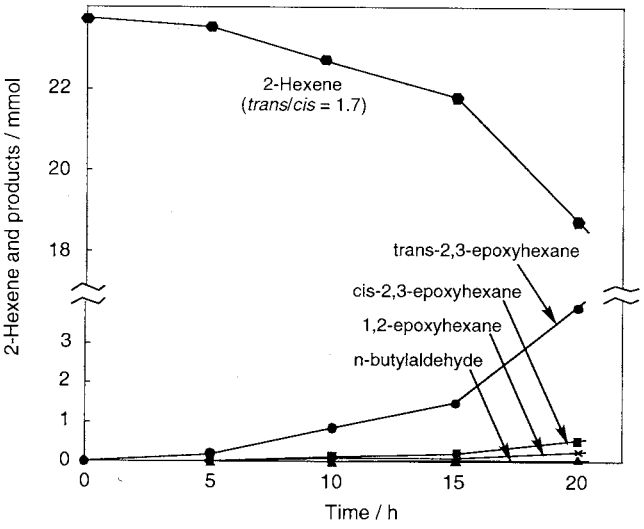

Figure 1. Formation of *trans*-2,3-epoxyhexane, *cis*-2,3-epoxyhexane, 1,2-epoxyhexane, and n-butylaldehyde as the result of photocatalytic reaction. The reaction was carried out in 2-hexene (*trans*/*cis* = 1.7, 2.0 g, 2.4 x 10^{-2} mol) using TiO_2 powder (Ishihara, PT-101, 20 mg) as the photocatalyst under a stream of oxygen.

Using any TiO_2 powders as the photocatalyst, 2,3-epoxyhexane was always obtained as the main product from 2-hexene, as shown in Figure 2. The highest efficiency of the generation of 2,3-epoxyhexane was obtained using TiO_2 (Japan Aerosil, P-25) as the photocatalyst. Using this catalyst, the chemical yield of the epoxide reached 83%. The average quantum efficiency of the epoxidation reaction was 7.0% for the photoirradiation for about 19 h. The efficiency becomes higher in the later period of the reaction as expected from the result of Figure 1.

Interestingly, the ratio of *trans*-2,3-epoxyhexane to *cis*-2,3-epoxyhexane produced by photoirradiation for 19 h using TiO_2 (Ishihara, PT-101) reached 7.1, which is about 4 times of the *trans*/*cis* ratio of the 2-hexene used as the starting material. The *trans* isomer was always the main product for 8 kinds of TiO_2

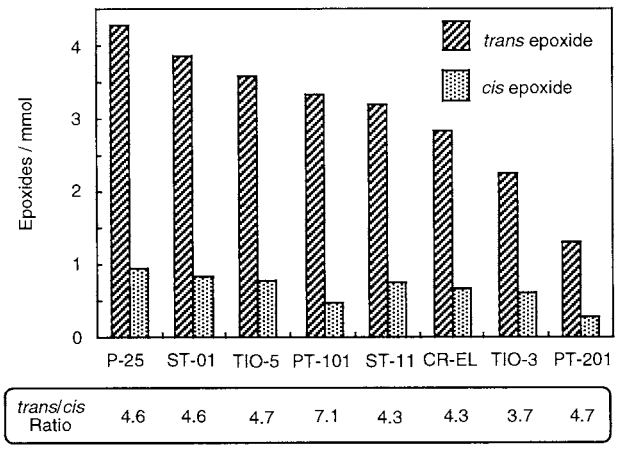

Figure 2. Comparison of the photocatalytic activities of different TiO_2 powders for producing *trans*-2,3-epoxyhexane and *cis*-2,3-epoxyhexane from 2-hexene (*trans/cis* = 1.7). The reactions were performed by photoirradiation for 19 h in pure 2-hexene (2.0 g, 2.4 x 10^{-2} mol) suspended with 20 mg TiO_2 powder under a stream of oxygen.

powders investigated, the ratio of *trans* to *cis* ranging from 3.7 to 7.1 as shown in Figure 2. The *trans* selectivity is considered to be related to the surface properties of the TiO_2 powders.

In order to clarify the stereochemistry of the epoxidation of 2-hexene, the reaction was carried out on the photoirradiated TiO_2 powder (Ishihara, PT-101) using *trans*-2-hexene and *cis*-2-hexene as the starting compounds. From *trans*-2-hexene, 2,3-epoxyhexane was obtained as a main product after photoirradiation of 19 h, with the ratio of *trans*- to *cis*-2,3-epoxyhexane being 63. The conversion yield of *trans*-2-hexene was 20.9 %, and the chemical yield of *trans*-2,3-epoxyhexane was 66 % based on the consumed amount of the starting material. In the case of *cis*-2-hexene, the *trans* to *cis* ratio of the epoxide was 0.14. The conversion yield was 5.2 % and the chemical yield of *cis*-2,3-epoxyhexane was 61%. These results indicate that the epoxidation of 2-hexene proceeds stereospecifically on the photoirradiated TiO_2 powder and the rate of photocatalytic epoxidation of *trans*-2-hexene was higher than that of the *cis* isomer.

The high yield of *trans*-2,3-epoxyhexane obtained from 2-hexene(*trans/cis* = 1.7) in the initial period of 19 h is, therefore, attributable to the higher reactivity of *trans*-2-hexene than *cis*-2-hexane on the photoirradiated TiO_2 and to the retention of the *trans* and *cis* configurations of the substrates during the epoxidation.

We have demonstrated that stereospecific photooxidation of 2-hexene proceeds on photoirradiated TiO_2 particles under a stream of oxygen. The reaction proceeds with high chemical yield and high quantum efficiency. We consider that the reaction system has a potential to be applied to practical syntheses of epoxide compounds.

This study was supported in part by the Iwatani Naoji Foundation.

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