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Solvent-free epoxidation using a tungstic acid catalyst on fluoroapatite

Junko Ichihara*

Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

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Abstract—Tungstic acid dispersed on fluoroapatite solid phase (H_2WO_4/FAp) catalyzed the epoxidation of cycloalkenes and allylic alcohols with a solid urea–hydrogen peroxide complex (urea–H_2O_2) without a solvent. © 2001 Elsevier Science Ltd. All rights reserved.

Recently, a number of novel solid catalysts and solid-supported catalysts have been developed for basic and important oxidation reactions of organic compounds.[1,2] And use of oxygen gas or aqueous hydrogen peroxide solution has been desired as the oxygen donor which has economic and environmental advantages. In most cases, the reactions are carried out in a heterogeneous system with liquid phase, and solvent-free reactions using solid phase have been rarely reported. We have constructed a new type of solid-phase-assisted epoxidation reaction system using solid tungstic acid (H_2WO_4) and a solid urea–hydrogen peroxide complex (urea–H_2O_2).[3–5] As the appropriate solid phase, we selected apatites, a biomaterial, because of their ion exchange ability and affinity for organic compounds. We now report that the combination of fluoroapatite (FAp) and the tungstic acid catalyst with solid urea–H_2O_2 is an effective reaction system for promoting epoxidation reaction on solid phase.

A heterogeneous epoxidation of cyclooctene using the tungstic acid catalyst on fluoroapatite (H_2WO_4/FAp, 0.20 mmol/g, 10 mol%) with urea–H_2O_2 was carried out as follows. To a solid mixture of FAp powder (0.50 g)[6] with urea–H_2O_2 powder (0.235 g, 2.50 mmol) was added tungstic acid powder (0.025 g, 0.10 mmol) in a test tube with a screw-cap, and mixed sufficiently. The solid mixture was permeated by a cyclooctene liquid (0.110 g, 1.0 mmol), and the mixture was left without stirring at room temperature. After 48 h the reaction smoothly proceeded to afford epoxycyclooctane in 90% yield. When tungstic acid was used alone, in contrast, the reaction sluggishly proceeded, as shown in Fig. 1. Since no reaction occurred with the use of only FAp, it was found that FAp had no catalytic activity for the oxidation with urea–H_2O_2.

The catalytic activity of H_2WO_4/FAp increased with increasing the FAp amount from 0.25 g to 1.0 g per 1 mmol of H_2WO_4, although the amount had an upper limit. Thus, for enhancing the catalytic activity it is important that the tungstic acid powder is more widely dispersed on the FAp solid phase. After mixing H_2WO_4/FAp with urea–H_2O_2 for 1 day at rt, dispersion of the catalyst on the FAp surface was observed by scanning electron microscopy.

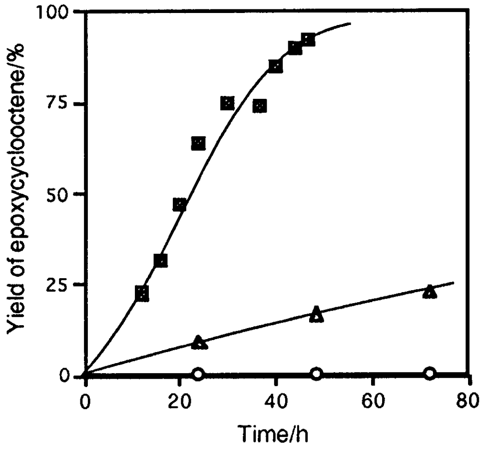

Fig. 1. Tungstate-catalyzed epoxidation of cyclooctene with urea–H_2O_2 at rt. (■) H_2WO_4/FA_P; (▲) H_2WO_4; (○) FAp.

Keywords: epoxidation; tungstic acid; fluoroapatite; solvent-free reaction.

* Corresponding author. Fax: +81-6-6879-8469; e-mail: ichihara@sanken.osakau.ac.jp

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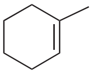
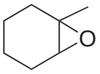
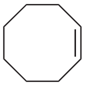
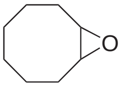
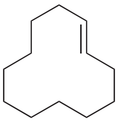
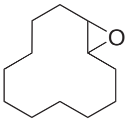
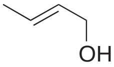
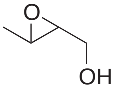
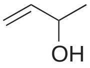
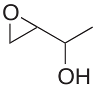
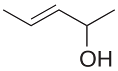
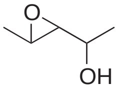
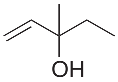
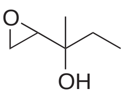
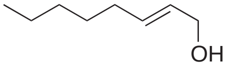
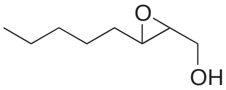
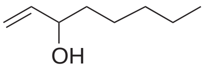
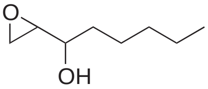
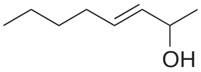
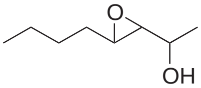
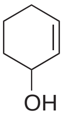
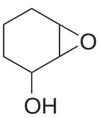
Table 1. Solvent-free epoxidation using the H_2WO_4/FAp catalyst[a]

Substrate	Time	Product	Yield/%[b]	erythro: threo[d]
	26 h		62	
	8 h		90[c]	
	4 d		70[c]	
	4 h		71	
	30 h		48[d,e]	77 : 23
	6 h		90	63 : 37
	7 d		78[c,f]	
	8 h		99	
	72 h		86[c,g]	73 : 23
	30 h		74	67 : 33
	3.5 h		49[d,h]	

[a] Substrate/H_2WO_4/FAp/urea·H2O2 = 0.5 mmol/0.05 mmol/0.25g/1.25 mmol at rt.

[b] Isolated yield unless otherwise noted.

[c] G.l.c. yield.

[d] Determined by ^1H NMR.

[e] The corresponding enone (8%) was also formed.

[f] Starting materials (22%) remained.

[g] The corresponding enone (10%) was also formed.

[h] The corresponding enone (34%) was also formed.

As well as FAp, such solids as silica gel, calcium fluoride, porous aluminum fluoride, and hydroxyapatite, etc., accelerated the epoxidation reaction. However, FAp was the most effective as a solid phase among them. Compared with the other solids, FAp is considered to assist the tungstic acid-catalyzed reactions as solid media moderately interacting with both the inorganic catalyst and alkenes. As expected, the surface phosphate ion of FAp crystal might be exchanged with the tungstate ion partially, when the tungstic acid catalyst was activated to peroxo-type by solid-phase reaction with solid urea–H_2O_2.

The epoxidations of some cycloalkenes and allylic alcohols using H_2WO_4/FAp and urea–H_2O_2 are summarized in Table 1. The epoxidation of the C=C double bonds of these compounds proceeded on and/or in solid phase at room temperature to afford the corresponding epoxides in good yields.

Our method using anhydrous hydrogen peroxide was performed under neutral conditions without a solvent and, thus, was preferable for the preparation of acid-sensitive or water-miscible epoxy-compounds consisting of 4 or 5 carbons. The epoxides were easily isolated via direct molecular distillation under vacuum from the reaction mixtures or extraction by *n*-hexane. Since tungstic acid-catalyzed epoxidations have been so far carried out with aqueous hydrogen peroxide under acidic conditions,[3,7,8] the formation of ring-opening products and difficulties of isolation are apt to occur. An improved method using a buffered solvent has been reported.[3] As regards diastereoselectivity for epoxidations of secondary allyl alcohols the solid-phase reaction showed similar preference but higher selectivity than those of aqueous liquid-phase reactions.[3,7,8]

In conclusion, not by use of solid catalysts which are rigidly and chemically bonded or impregnated to the solid surface but by both use of weak interaction of the catalyst with the solid surface and dispersion by activating the catalyst, we have succeeded in the tungstic acid-catalyzed epoxidation on the FAp solid phase without a solvent under mild conditions. The solvent-free organic reaction system using solid phase should be an attractive method for an environmentally friendly-catalyzed organic reaction system. Further studies along this line with other tungstates and molybdates catalysts and the possibilities of the method are in progress.

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