

Hydrotalcite-Catalyzed Epoxidation of Olefins Using Hydrogen Peroxide and Amide Compounds

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Selective and efficient epoxidations of olefins have been extensively studied because of versatile intermediates of epoxides in various organic syntheses.¹ Aqueous H₂O₂ is an ideal oxidant, because it is a cheap and safe oxidant, and easy to handle, giving only water as a coproduct. Heterogeneous organic reactions, especially using mineral catalysts such as zeolites,² montmorillonites,³ and hydrotalcites,⁴ have received much attention due to the following advantages: (i) easy separation from the reaction mixture, (ii) reusable catalysts, (iii) easy modification of their surface and pore, and (iv) use of nonpolluting natural minerals. Therefore, epoxidations using hydrogen peroxide by the above solid catalysts can contribute to the strong demand of environmentally benign chemical processes.⁵ Recently, we found that layered hydrotalcites could efficiently catalyze various oxidation reactions; the basic hydroxyl groups in the surface of the Brucite-layer promoted these reactions.^{6–8} In our previous epoxidation using a combined oxidant of H₂O₂ and nitriles catalyzed by hydrotalcites, the nitriles were converted to amides via peroxycarboximidic acid intermediates.⁶ It can be expected that the resultant amides could be further employed for the epoxidation reaction to develop the epoxidation system with high atom economy.⁹ Here, we report an efficient method for the heterogeneous oxida-

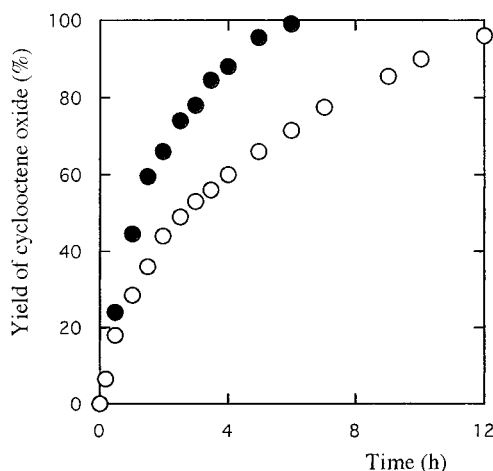
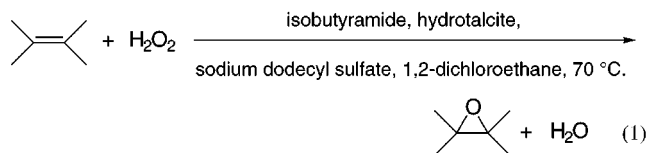


Figure 1. Reaction profile of the Mg₁₀Al₂(OH)₂₄CO₃-catalyzed epoxidation of cyclooctene with (●) and without (○) sodium dodecyl sulfate. Reaction conditions: cyclooctene (4 mmol), isobutylamide (6 mmol), Mg₁₀Al₂(OH)₂₄CO₃ (0.05 g), 30% aq H₂O₂ (0.9 mL, 8 mmol), sodium dodecyl sulfate (0.2 mmol).

tion of various olefins to the corresponding epoxides using H₂O₂ and amides catalyzed by hydrotalcites in the presence of an anionic surfactant (eq 1).



Amides, H₂O₂, and hydrotalcites were indispensable components for our epoxidation system. Among amides used, isobutylamide was found to be the most effective for this epoxidation.¹⁰ As shown in Figure 1, adding an anionic surfactant of sodium dodecyl sulfate to the above oxidation system remarkably accelerated the epoxidation rate. In contrast, the use of cationic surfactants, e.g., cetylpyridinium chloride monohydrate and dodecyltrimethylammonium bromide, strongly inhibited the epoxidation. Nonionic surfactants, e.g., sorbitan monolaurate and octyl phenoxy polyethoxyethanol, did not remarkably influence the epoxidation rate. In epoxidation of cyclooctene, 1,2-dichloroethane, benzene, toluene, and cyclohexane were good solvents to give 73, 67, 65, and 58% yields of cyclooctene oxide for 3 h, respectively. On the other hand, methanol and 2-propanol as water-miscible solvents were poor for the epoxidation. Table 1 shows the oxidation of cyclooctene using various kinds of base catalysts in the presence of sodium dodecyl sulfate. The yields of cyclooctene oxide increased with increasing the heat of benzoic acid adsorption on hydrotalcites (entries 1–4). The calorimetric heat of benzoic acid adsorption is a measure of the basicity of the solid surfaces.^{7d} The catalytic activity of MgO was lower than those of hydrotalcites although MgO possesses a moderate basicity

(10) In the epoxidation of 1-octene using Mg₁₀Al₂(OH)₂₄CO₃, the following reactivity of amides was observed: isobutylamide(6.8) > pivalamide(5.6) > n-valeramide(4.8) > propionamide(2.9) > benzamide(2.4) > acetamide(1.0). The values in parentheses are relative rates for the epoxidation, which are normalized to that of acetamide.

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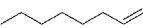
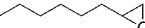
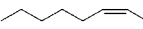
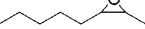
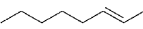
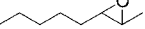


















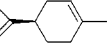
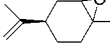
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Table 1. Epoxidation of Cyclooctene Catalyzed by Various Catalysts Using H₂O₂ and Isobutyramide^a

entry	catalyst	conversion of cyclooctene ^b (%)	yield of cyclooctene oxide ^b (%)	heat of adsorption ^c (J g ⁻¹)
1	Mg ₁₀ Al ₂ (OH) ₂₄ CO ₃	76	73	14.2
2	Mg ₅ Al(OH) ₁₁ CO ₃	65	63	8.1
3	Mg ₆ Al ₂ (OH) ₁₆ CO ₃	49	44	6.3
4	Mg ₆ Al ₂ (OH) ₁₆ SO ₄	24	24	5.1
5 ^d	MgO	23	23	8.4
6	Mg(OH) ₂	33	30	6.4
7	Al(OH) ₃	24	23	1.8
8 ^e	NaOH	12	4	—
9	without	8	8	—

^a Reaction conditions: olefin (4 mmol), isobutyramide (6 mmol), catalyst (0.05 g), 1,2-dichloroethane (10 mL), 30% aq H₂O₂ (0.9 mL, 8 mmol), sodium dodecyl sulfate (0.2 mmol), 70 °C, 3 h. ^b Determined by GC using an internal standard technique. ^c See ref 7d. ^d MgO calcined at 400 °C was used. ^e NaOH was equivalent to the amount of hydroxyl functions in hydrotalcites (1.5 mmol).

Table 2. Epoxidation of Various Olefins Catalyzed by Mg₁₀Al₂(OH)₂₄CO₃ Using H₂O₂ and Isobutyramide^a

entry	olefin	product	time (h)	conversion of olefin (%) ^b	yield (%) ^b
1 ^c			24	89	80
2			6	92	90
3			6	93	93
4 ^d			18	91	91(88)
5			8	100	>99
6			12	98	94(93)
7			6	97	96(86) (only <i>exo</i>)
8			6	100	>99(91)
9			8	96	95(90)
10			15	99	95(98)
11 ^e			12	97	81
12 ^e			12	87	84
13 ^e			6	99	86

^a Reaction conditions: olefin (4 mmol), isobutyramide (6 mmol), Mg₁₀Al₂(OH)₂₄CO₃ (0.05 g), 1,2-dichloroethane (10 mL), 30% aq H₂O₂ (0.9 mL, 8 mmol), sodium dodecyl sulfate (0.2 mmol), 70 °C. ^b Determined by GC using internal standard technique. Values in parentheses are isolated yields. In the case of the isolation experiments, the reaction scale was three times as much as that of reaction conditions a. ^c Reaction conditions: olefin (4 mmol), isobutyramide (40 mmol), Mg₁₀Al₂(OH)₂₄CO₃ (0.15 g), 1,2-dichloroethane (10 mL), 30% aq H₂O₂ (4.5 mL, 48 mmol), sodium dodecyl sulfate (0.2 mmol), 70 °C. ^d Substrate: *cis/trans* = 44/56, product: *cis/trans* = 41/59. ^e Propionamide (12 mmol) was used instead of isobutyramide. Small amounts of terminal epoxides and diepoxides were also formed.

(entry 5). These results indicate that Brønsted basic sites derived from surface hydroxyl groups on hydrotalcites might play an important role in this epoxidation. Further, NaOH was not an effective base under our conditions.

Table 2 shows the epoxidation of various olefins using H₂O₂ and isobutyramide in the presence of the Mg₁₀-Al₂(OH)₂₄CO₃. Remarkably, our oxidation system exclusively gave epoxides without other oxidation products. In cyclooctene, the yield of cyclooctene oxide based on consumed H₂O₂ attained 84%. Common olefins gave excellent yields of the corresponding epoxides with almost a stoichiometric amount of isobutyramide (entries 2–10).

On the other hand, in the case of a terminal olefin like 1-octene, a large excess of the amide was necessary to attain a high yield of the epoxide (entry 1). This epoxidation proceeded stereospecifically with a retention of the configuration of double bonds (entries 2–4). The regioselectivity in the epoxidation of olefins having different types of double bonds was strongly dependent on amides used. For an example, 4-vinyl-1-cyclohexene was oxidized to form 1,2-epoxy-4-vinylcyclohexane with 97% selectivity in the case of propionamide, while the use of isobutyramide gave the 1,2-epoxide in 84% selectivity (entries 11 and 12). The above exclusive formation of the 1,2-epoxide

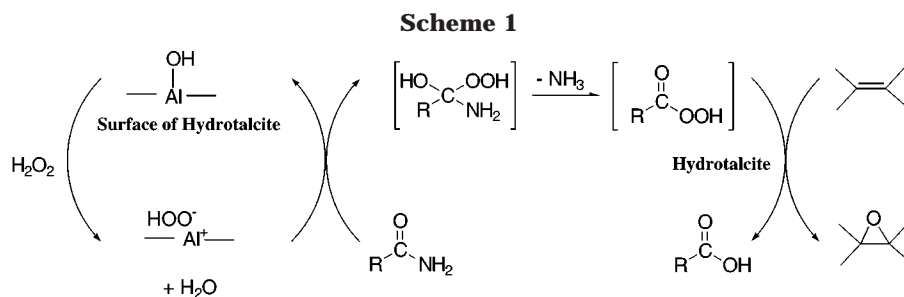


Table 3. Recycling of the $\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$ Catalyst in the Epoxidation of Cyclooctene^a

recycle no.	conversion of cyclooctene ^b (%)	yield of cyclooctene oxide ^b (%)
fresh	100	>99
1	99	97
2	99	98
3	97	94

^a Reaction conditions: olefin (4 mmol), isobutyramide (6 mmol), $\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$ (0.05 g), 1,2-dichloroethane (10 mL), 30% aq H_2O_2 (0.9 mL, 8 mmol), sodium dodecyl sulfate (0.2 mmol), 70 °C, 6 h. ^b Determined by GC using an internal standard technique.

was also observed with the combined oxidant consisting of molecular oxygen and isobutyraldehyde.¹¹ The relative epoxidation rate of (*Z*)- and (*E*)-2-octene was 1.2, which closely resembles that using *m*-CPBA. Therefore, this epoxidation might occur via peracids as active intermediate oxidants.¹²

Here we represent a possible scheme of this epoxidation. H_2O_2 attacks a basic hydroxyl function on the surface of hydrotalcites to form an HOO^- species, which reacts with an amide to generate a peracid together with NH_3 in the aqueous phase. Further, the oxygen transfer from the peracid to an olefin occurs at the surface boundary between aqueous and organic phases. In a separate experiment on the oxidation of 1-octene using *m*-CPBA, the hydrotalcite catalyst promoted the formation rate of the epoxide twice. The above phenomena show that the hydrotalcite can catalyze not only the formation step of the HOO^- species, but also the oxygen transfer step from the peracid to an olefin. *Vide supra*, in the absence of the surfactant, attaining a high yield of epoxides necessitated prolonged reaction time. This epoxidation occurred in three phases; an olefin is in the organic phase, while hydrogen peroxide, amide, and solid hydrotalcite are in the aqueous phase. The main roles of the above surfactant are (i) to increase the contact area of the interface between the aqueous and organic phases and (ii) to enhance the transfer of a lipophilic olefin from the organic phase to the interface between the above two phases.

Use of solid hydrotalcites could make the workup procedures very simple. The hydrotalcites were easily separated from the reaction mixture by a filtration. Further, the $\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$ was reused in the epoxidation of cyclooctene. The results were shown in Table 3. The high catalytic activity and selectivity were maintained even after third reuse.

In conclusion, hydrotalcites act as base catalysts for the epoxidation of various olefins using H_2O_2 and amides under mild reaction conditions and are reusable without an appreciable loss of the catalytic activity and selectiv-

ity. The anionic surfactants can accelerate the rate of the triphasic epoxidation using aqueous H_2O_2 as an oxidant. We have continuously designed the hydrotalcite catalyst systems for developing many environmentally friendly reactions.

Experimental Section

General. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Mg}(\text{OH})_2$ were purchased from Wako Pure Chemical as special grade. MgO was supplied from the Catalysis Society of Japan as a reference catalyst, JRC-MgO-#1000 and used after the calcination at 400 °C. Hydrogen peroxide (about 30%) and surfactants were purchased from Wako Pure Chemical and used as received. *m*-CPBA was purchased from Nakalai Tesque and used without further purification. Olefins, amides, and solvents were purified by the standard procedures before use.¹³ All of the epoxidation products were identified by mass spectroscopy, ¹H NMR spectra, and infrared spectra.

General Procedure for Preparation of Hydrotalcite Catalysts. Various hydrotalcites were prepared by the literature procedure.¹⁴ A typical example is for $\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.01 mol) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.05 mol) were dissolved in water (100 mL). A second water solution (60 mL) of Na_2CO_3 (0.03 mol) and NaOH (0.07 mol) was prepared. The first solution was slowly added to the second. The resulting mixture was heated at 65 °C for 18 h with vigorous stirring. The white slurry was then cooled to room temperature, filtered, washed with large amount of water, and dried overnight at 110 °C. The basal spacing was 7.93 Å determined from the XRD measurement.

Measurement of the Basicity of Catalysts.^{7d} The calorimetric heats of benzoic acid adsorption on the catalysts were measured by using a micro differential scanning calorimeter. Catalyst (10 mg) was added to a cyclohexane solution (0.5 mL). The solution of benzoic acid (0.005 mmol) in cyclohexane (0.2 mL) was added to the above solution. The heats generated from this solution correspond to the calorimetric heats of benzoic acid adsorption.

General Procedure for the Epoxidation with Hydrotalcite Catalysts. To a reaction vessel with a reflux condenser were successively added the hydrotalcite of $\text{Mg}_{10}\text{Al}_2(\text{OH})_{24}\text{CO}_3$ (0.15 g), 1,2-dichloroethane (30 mL), olefin (12 mmol), isobutyramide (18 mmol), sodium dodecyl sulfate (0.6 mmol), and 30% aqueous H_2O_2 (2.7 mL, 24 mmol). After the resulting mixture was stirred at 70 °C for an appropriate time, the hydrotalcite was separated by filtration. The filtrate was treated with aqueous Na_2SO_3 solution, followed by extraction with 1,2-dichloroethane (25 mL \times 3). The extract was concentrated and subjected to column chromatography on silica gel (Wako gel C-200) with a mixture of *n*-hexane and ether (10:1), which afforded pure epoxides.

Recycling of the Hydrotalcite Catalyst for the Epoxidation of Cyclooctene. The first run using cyclooctene (4 mmol) was carried out using the same procedure as described in the above. The isolated hydrotalcite was calcined at 400 °C and further treated with 5 wt % aqueous Na_2CO_3 solution before reuse. These recycling procedures were repeated three times in the same manner as in the first recycle.

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