A New and Direct Synthesis of Lactic Acid from Acrylic Acid Using an Excimer Laser with High Intensity

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A new and direct method of XeF (351 nm) laser irradiation of acrylic acid **1** solution containing H_2O_2 are described for the chemical synthesis of lactic acid **2**. Increase in the yield strongly depended on the irradiation dose and H_2O_2 feeding rate, and the formation of **2** showed the quantum yield, 0.3, and the selectivity, 50%, at the maximum yield. Product analysis indicated that OH radicals formed with high density by the laser-photolysis of H_2O_2 are equally bonded to the carbons of α- and β-positions of **1** to produce **2** and 3-hydroxypropanoic acid with ratio of 1 to 1.

Lactic acid **2** is very important as raw materials for the brewing and the food industries,[1,2] and especially the uses of its polymer as biodegradable and biocompatible materials[3,4] are of growing importance in biomedical field etc. At present, **2** is mainly manufactured by the zymotechnics and chemical synthetic methods, and of them, the latter is a complex and multistep process using acetaldehyde as a starting material. Even in the catalytic oxidation of acrylic acid **1** with osmium tetraoxide using chlorate as a cooxidizing agent, which is an example of such an investigation, the main product is 2,3-dihydroxypropanoic acid, dihydroxylated adduct of **1**.[5] Thus, the chemical direct synthesis has scarcely been investigated. Under the circumstances that the demand of **2**, on the whole, would continue to expand, it is much expected to develop a new and easier direct synthetic method of **2**. For this, we have attempted to synthesize directly **2** from acrylic acid **1** using an excimer laser with high intensity. We describe here a new direct synthetic method of **2** from **1** containing H_2O_2 with a XeF laser.

The N_2-saturated aqueous solution of **1** (20 mM)[6] was irradiated with a XeF laser (351 nm)[7] at room temperature. Under irradiation, the aqueous 30% H_2O_2 was added to the solution at the feeding rate from 3.7 to 14.7 mℓ h^{-1}. The irradiated solution was analyzed by chromatographic method.[8]

When the N_2-saturated **1** containing H_2O_2 was irradiated with the XeF laser, **2**, 3-hydroxypropanoic acid **3**, 2,3-dihydroxypropanoic acid **4** and propanoic acid **5** were produced together with trace amounts of formic **6** and acetic **7** acids (Figure 1). On the other hand, when the N_2-saturated **1** alone was irradiated in the absence of H_2O_2, these products were hardly observed even after prolonged irradiation leaving behind the unchanged **1**. Also, gaseous products such as H_2, CO_2 etc. were not detectable. These facts indicate that the decomposition and the polymerization of **1** by the laser irradiation do not occur in this system. From these results, it was found that the presence of H_2O_2, not H_2O, is an essential condition for the efficient formation of **2**.

Figure 2 shows the concentration of products as a function of absorbed energy at 14.7 mℓ h^{-1} of H_2O_2 feeding rate. As shown, **2** and **3** are main products. On the other hand, the concentration of **4** was less than 1/10 of those of **2** and **3**. Also, **5** was formed in extremely small quantities, still smaller

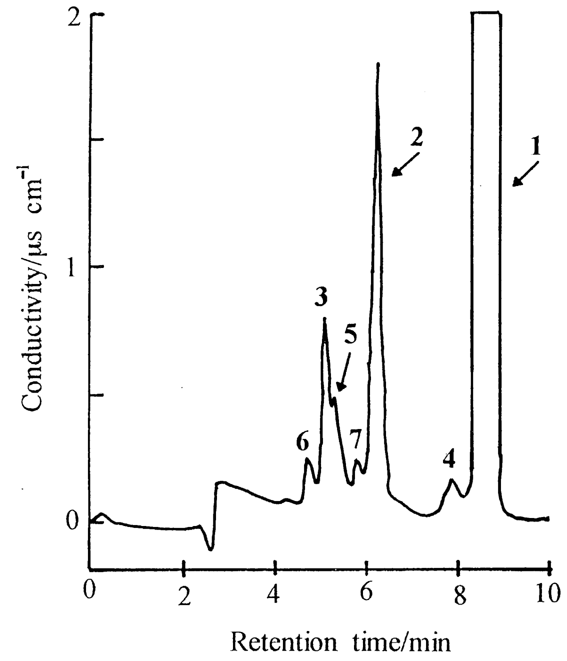

Figure 1. Ion chromatogram of the reaction mixture of **1** containing H_2O_2 irradiated with a XeF laser.

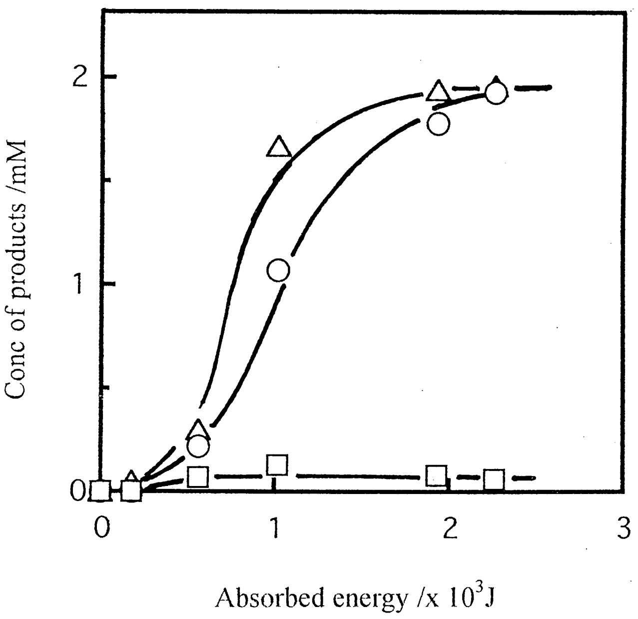

Figure 2. The dependence of the product concentrations for **2** (○), **3** (△), and **4** (□) on the absorbed energy at H_2O_2 feeding rate of 14.7 mℓ h^{-1}.

than 4. Furthermore, the concentrations of both **2** and **3** increased rapidly with absorbed energy, and then reached almost to a constant value to be saturated at absorbed energy of about 2.3 x 10^3 J although the concentration of **3** was somewhat larger than that of **2** in the intial stage of the reaction. Also, similar results were obtained at different H_2O_2 feeding rates.

Figure 3 shows the concentration of main products as a function of H_2O_2 feeding rate at absorbed energy of 2.3 x 10^3 J giving the maximum yield. As seen, the concentrations of both **2** and **3** increased with H_2O_2 feeding rate, and then reached almost to a constant value at H_2O_2 feeding rate of 14.7 $m\ell\ h^{-1}$. It is noteworthy that those were always equal one another at the same H_2O_2 feeding rate, indicating that **2** and **3** are formed with molar ratio of 1 to 1. The conversion of **1** into **2** and **3** was about 10% at H_2O_2 feeding rate of 14.7 $m\ell\ h^{-1}$ in this case. Also, the quantum yield and the selectivity for the formation of **2** were 0.3 and 50%, respectively. Therefore, it was evidently shown that **2** is directly synthesized from **1** in the presence of H_2O_2 using a XeF laser with high intensity. Thus, only the hydroxylation process proceeds in this system, so that the hydroxylated adducts (**2** and **3**) of **1** are efficiently produced with total quantum yield of 0.6.

H_2O_2 shows a broad absorption spectrum in the range of the wavelength of 351 nm, while **1** does not show.[9] As described already, organic products were not produced by the irradiation of **1** alone. It can therefore be considered that OH radical [$\Phi(\cdot OH) \approx 2$] formed efficiently by the decomposition of H_2O_2 by XeF laser irradiation[10] is an initiating species to produce **2** in this system. This consideration is also supported from the result that the formation of **2** was strongly suppressed by the addition of potassium thiocyanate, which is an efficient scavenger of OH radical.[11] Furthermore, in this reaction, **2** and **3** were main products as shown in Figure 3, and their yields were apporoximately even, indicating that OH radicals formed with high density by the laser-photolysis of H_2O_2 are equally bonded to the carbons of α- and β-positions of **1** to produce **2** for α and **3** for β, respectively.

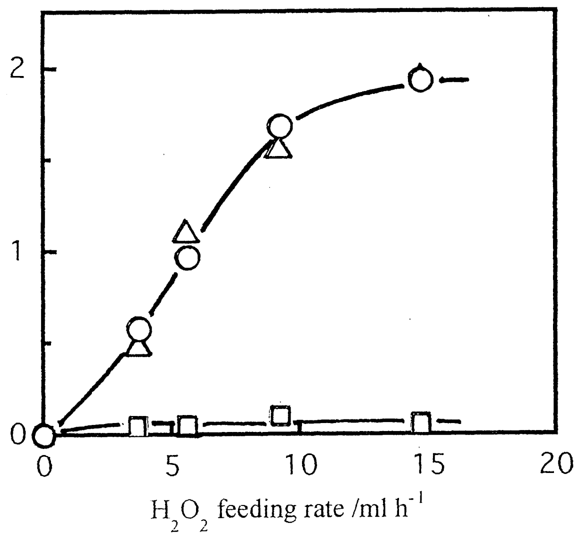

Figure 3. The dependence of the product concentrations on the H_2O_2 feeding rate at absorbed energy of 2.3 x 10^3 J. Symbols are the same as those of Figure 2.

It is well known that in the case of **1**, in which the electron-withdrawing group such as carboxyl one is conjugated with the C-C double bond, the carbon of β-position is much more subject to attack by anionic species than that of α-position. Similarly, this orientation of addition has been also recognized in the radical addition to alkenes from the predominant reaction of the β-position based on the steric effects mainly.[12] In practice, also in this case, as shown in Figure 2, the concentration of **3** is much larger than that of **2** in the initial stage of reaction. However, as mentioned above, the reaction eventually approaches an equilibrium state to produce equimolecular quantities of **2** and **3**. Such an orientation of addition with ratio 1 to 1 of ·OH to the carbons of α- and β-positions of **1**, as shown in Figure 3, may be attributed to the relatively small size of ·OH and/or the use of less hindered unsubstituted **1**.[13]

References and Notes

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6 The laser-induced reactions were carried out in a Pyrex glass cylindrical vessel (volume: 91.5 $m\ell$, diameter: 35.5 mm, light pathlength: 70 mm) with a Suprasil window for the incidence of laser beam.

7 Lumonics Hyper EX-460, initial power: 2.9 W, frequency: 16 Hz, pulse duration: 12 - 15 ns, beam shape: 9 x 34 mm.

8 Ion chromatograph (Yokogawa IC-100, column: SAX1 two, eluent: 15 mM$Na_2B_4O_7$) and gas chromatograph (Shimadzu GC-7A, Porapak Q; GC-4C, Porapak N; GC-3BT, Molecular sieve 5A) were used.

9 UV-spectra were recorded on a Shimadzu UV-2100 spectrophotometer.

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