

LASER-INDUCED PHOTOCHEMICAL REACTION OF MALEIC ACID SOLUTIONS IN THE PRESENCE OF HYDROGEN PEROXIDE

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Targeting the selective and direct synthesis of tartaric acid (TA), the photochemical reactions of maleic acid (MA) solutions containing H₂O₂ in various solvents have been investigated using four wavelengths in the UV region between 193 and 351 nm, with high intensity from an excimer laser. All the laser irradiations in H₂O resulted in the direct synthesis of TA with lower selectivity and it was found that, with XeF-laser (351 nm) irradiation in 1,4-dioxane, TA is selectively and directly synthesized from MA containing H₂O₂ of lower concentration at room temperature. On the other hand, none of the irradiations in methanol, N,N-dimethylformamide, acetonitrile, and tetrahydrofuran gave the selective formation of TA. On the basis of these results, the reaction scheme for the selective formation of TA is discussed.

Keywords: Organic photosynthesis; excimer laser; tartaric acid; selectivity; wavelength effects; solvent effects

1. INTRODUCTION

Since the beams of the UV region emitted from an excimer laser are monochromatic and of high intensity and, moreover, their photon

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energies are nearly comparable to the bond energy of some organic compounds [1], they enable efficient formation of a desired active species with high density for organic chemical reactions. Therefore, the application of the laser in organic chemical reactions is a promising methodology for the direct and selective synthesis of valuable compounds [2]. From such viewpoints, many studies on the laser-induced organic chemical reactions have been carried out [3]. As an example, as reported previously, we found that diols are directly and selectively synthesized by the laser irradiation of N_2 -saturated alcohols containing H_2O_2 [4], and demonstrated that more reactive hydroxyl radicals are easily and purely formed with high density by excimer-laser irradiation of H_2O_2 because of the high intensity compared with the case of UV lamp irradiation [4, 5].

Tartaric acid (TA) is very important as an intermediate for the manufacture of medicines, and also in the food industry. At present, TA is industrially manufactured by a very complex synthetic method from tartar [6]. In laboratories, it is mainly prepared by oxidizing maleic acid (MA) using osmium tetroxide [7, 8]. However, the catalyst is poisonous and expensive, furthermore, prolonged reaction time is required for this process. For these reasons, a simpler, more rapid, and practical methodology for the synthesis of TA was eagerly sought [8, 9]. The above process newly developed by us is a selective and direct formation route of the hydroxyl group which is a useful functional group and may be applicable to some compounds such as alkene as a selective and direct introduction method of the hydroxyl group in the double bond. We have, therefore, attempted to induce efficiently the addition of the hydroxyl radicals formed by laser-photolysis of H_2O_2 to the double bond in MA, for the purpose of the selective and direct synthesis of valuable compounds such as TA containing a hydroxyl group. On the other hand, the laser-induced photochemical reaction of an aqueous solution of MA has been investigated from the viewpoint of chemistry in excited molecular electronic states relative to nonlinear laser chemistry [10, 11], these studies showed that the basic process is cis-trans isomerization leading to the formation of fumaric acid (FA) with the dimerization, etc. However, there is as yet very little information on the study of the laser-induced photochemical reaction of MA for the synthesis of more valuable compounds. We, therefore, have investigated in detail the

effects of reaction conditions, especially the effects of H_2O_2 feeding rate, wavelength of laser beams and solvents, on the formation of TA from MA. In this paper, we report a new method for the direct and selective synthesis of TA from MA initiated by XeF laser-photolysis of H_2O_2 .

2. EXPERIMENTAL

All chemicals were of reagent grade. MA and all solvents such as 1,4-dioxane (DO), methanol (MeOH), N,N-dimethylformamide (DMF), acetonitrile (MeCN), and tetrahydrofuran (THF) were purchased from Nakalai Tesque Co., Ltd., and from Tokyo Kasei Kogyo Co., Ltd., respectively, and were used without further purification. These solvents and distilled water were selected from the viewpoint that they all dissolve MA at room temperature, and also are miscible with aqueous H_2O_2 . Furthermore, all these solvents show absorption bands in the wavelength range shorter than 300 nm. The 30% aqueous solution of H_2O_2 was purchased from Santoku Chemical Industries Co., Ltd. N_2 used was of high purity grade of above 99.9%.

The laser-induced reactions were carried out in a Pyrex glass cylindrical reaction vessel (volume: 91.5 ml, diameter: 35.5 mm, light pathlength: 70 mm) with a Suprasil window (diameter: 45 mm, thickness: 3 mm) for the incidence of laser beams. Water, DO, and their mixtures, MeOH, DMF, MeCN, and THF solutions of MA were placed in the reaction vessel, respectively, and well-bubbled with N_2 in order to remove oxygen. The N_2 -saturated solution of MA was stirred magnetically (500 rpm), and mainly irradiated with the XeF laser (Lumonics Hyper EX-460, wavelength: 351 nm, pulse energy: 80 mJ per pulse, frequency: 16 Hz, pulse duration: 12–15 ns, beam shape: 9×34 mm) at room temperature. At the same time with irradiation, a 30% aqueous solution of H_2O_2 was added to the solutions of MA with the feeding rate from 3.4 to 13.1 ml h^{-1} by using a microfeeder (Atto Corp., AC-2120). The quantity of light from the lasers was determined by using a calorimeter (Scientech 38-4UV5). The calorimeter was also placed behind the reaction vessel to determine precisely the quantity of light absorbed in the system during the laser irradiation. Furthermore, for the experiments of wavelength effects on the photochemical

reaction, especially the formation of TA, ArF (wavelength: 193 nm, energy: 2.4 W), KrF (wavelength: 248 nm, energy: 2.9 W), XeCl (wavelength: 308 nm, energy: 2.1 W), and XeF (wavelength: 351 nm, energy: 2.2 W) lasers were used with irradiation of an aqueous solution of MA containing H₂O₂.

Analyses were mainly carried out by ion chromatography (Yokogawa IC-100, SAX1 column, length: 25 cm, two) and by gas chromatography (Shimadzu GC-3BT, Molecular sieve 5A column and GC-4C, Porapak N column) for gaseous products. A gas chromatograph-mass spectrometer (Shimadzu QP-5000, DB-1 column) was also used. The UV absorption spectra were recorded with a Shimadzu spectrophotometer (UV-2100). The pH of the solutions before and after the irradiation was obtained by measurements with a Horiba pH meter (F-15).

3. RESULTS

H₂O₂ has an absorption band in the wavelength around 350 nm, while MA does not have it in that range. So, firstly, the XeF laser (351 nm) was used as the source of beam absorbed by H₂O₂ but not by MA, to avoid the decomposition of MA. In fact, when the N₂-saturated aqueous solution of MA alone was irradiated in the absence of H₂O₂, organic products were hardly produced even on irradiation for 45 min, indicating that the decomposition does not occur. On the other hand, as shown in Figure 1, when the N₂-saturated aqueous solution of MA was irradiated with the XeF laser at H₂O₂ feeding rate of 3.6 ml h⁻¹, glycolic acid (GA) was produced as the main product together with TA, FA, oxalic, succinic, and malic acids as minor products, and small amounts of gaseous products such as H₂, CO, and CO₂ etc. In sharp contrast to XeF-laser irradiation, negligible amounts of TA were detected by irradiation with UV light (mainly 366 and 334 nm, ca. 13 mW/cm²) from an Hg lamp obtained through the UV filter (Toshiba UV-33 and UV-D33S), even on irradiation for ca. 20 h. It was found from these results that the quantity of TA was much larger in the laser irradiation than in the lamp irradiation. This indicates that the laser irradiation is more favorable for the efficient formation of TA although the wavelength and the irradiation dose of the laser beams

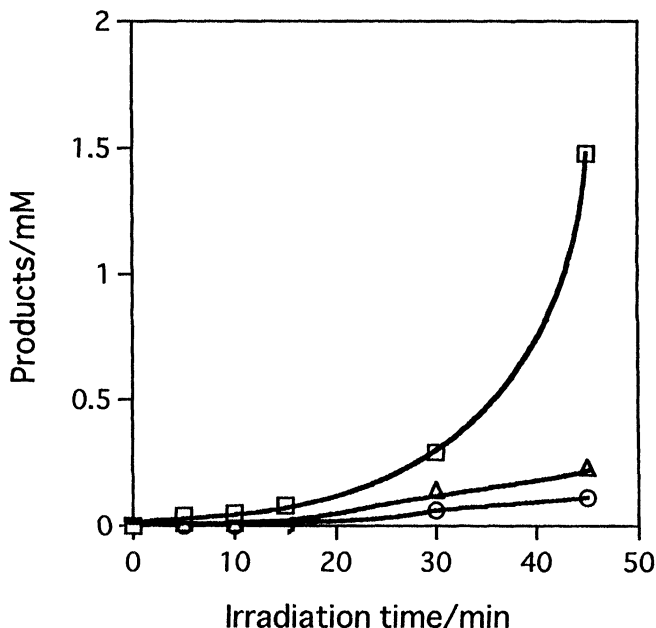


FIGURE 1 Plots of the quantities of main products as a function of irradiation time. Aqueous 30% H_2O_2 feeding rate: 3.6 ml h^{-1} . \square : GA, \circ : TA, \triangle : malic acid.

are almost the same as those of the UV light. For this reason, it can be considered that the light intensity per unit time is about 10^7 times larger with the laser than with the lamp, i.e., high intensity for the laser, as described already. Also, as shown in Figure 1, the quantity of TA gradually increases with irradiation time, while the quantity of GA increases steeply and quadratically with time, giving the quantum yield of ca. 0.1 for 45 min irradiation. The selectivity of TA formation of 45 min irradiation was about 6%. In contrast, at H_2O_2 feeding rate of 13.1 ml h^{-1} , the selectivity of TA was very much smaller ($<1\%$). Thus, it was revealed that TA formation is favorable in lower H_2O_2 feeding rate. Furthermore, the selectivity of TA formation in this reaction was smaller and the main product was GA, not TA. However, GA is also a series of hydroxy acids, which are obtained via the mono- or dihydroxylation of MA in this system, in analogy with TA. Moreover, as judged from the structural formula, it may be presumed that GA is a secondary product resulting from the decomposition by

the laser-reirradiation with the high intensity of TA once formed in this reaction. From this viewpoint, in an attempt to suppress the secondary decomposition of TA, the effects of the wavelengths of laser beams on the formation of hydroxy acids, including TA, were examined next, using the fourth wavelengths of the UV region of 193 to 351 nm from the excimer laser.

Table I shows the wavelength effects on the quantities of main products from an aqueous solution of MA by ArF-, KrF-, XeCl-, and XeF-laser irradiations for 45 min at H₂O₂ feeding rate of 3.8 ml h⁻¹. In the case of ArF-laser (193 nm) irradiation, GA is the main product, and the selectivity of TA formation was about 6%, similarly with the XeF irradiation. However, the combined selectivity of hydroxy acid was about 72%, much lower than in the case of XeF irradiation (92%). On the other hand, in KrF-laser (248 nm) irradiation, FA formed by the isomerization via the direct absorption excitation of MA is the main product (selectivity, ca. 50%), and the selectivity of TA was nearly zero. Also, in XeCl-laser (308 nm) irradiation, FA formed by the isomerization via the two-photon absorption excitation of MA was the main product (selectivity, ca. 46%) although the quantity of TA was the largest among the wavelengths used, and the combined selectivities of hydroxy acid for both KrF- and XeCl-laser irradiations were below 50%. In sharp contrast, a very high combined selectivity of hydroxy acid in XeF-laser irradiation indicates that only negligible amounts of products other than hydroxylated products of MA are produced. From these results, it was apparent that laser-induced photochemical reactions of an aqueous solution of MA containing H₂O₂ are significantly affected by the wavelengths of laser

TABLE I Comparison of the quantities of products under the laser irradiations^a

<i>Product</i>	<i>XeF</i>	<i>ArF</i>	<i>KrF</i>	<i>XeCl</i>
GA	1.48	5.73	0.86	2.22
TA	0.11	0.65	0.01	1.76
FA	0.03	0.02	3.55	3.81
Malic acid	0.23	1.07	2.64	0
Succinic acid	0	1.56	0	0
Oxalic acid	0.08	1.35	0.13	0.46

^a[Product]: mM, irradiation time: 45 min, H₂O₂ feeding rate: 3.8 ml h⁻¹.

beams, indicating the usefulness of the XeF laser for the efficient formation of the hydroxylated products including TA.

As mentioned above, it has been confirmed that an efficient formation of the hydroxylated products is strongly dependent on the wavelengths of laser beams. However, the results of the wavelength effects suggest that the laser-induced secondary decomposition of TA once formed is not necessarily responsible for the formation of GA, and that the effects of other reaction conditions must also be taken into consideration for the formation. We, therefore, examined the effects of solvents on the selective formation of TA as a reaction factor, using the XeF laser. Here, DO in the place of H₂O, a polar solvent, was used as a nonpolar solvent under the solvent selection conditions previously described in the experimental section in this text. Figure 2 shows the quantities of main products from a solution of MA

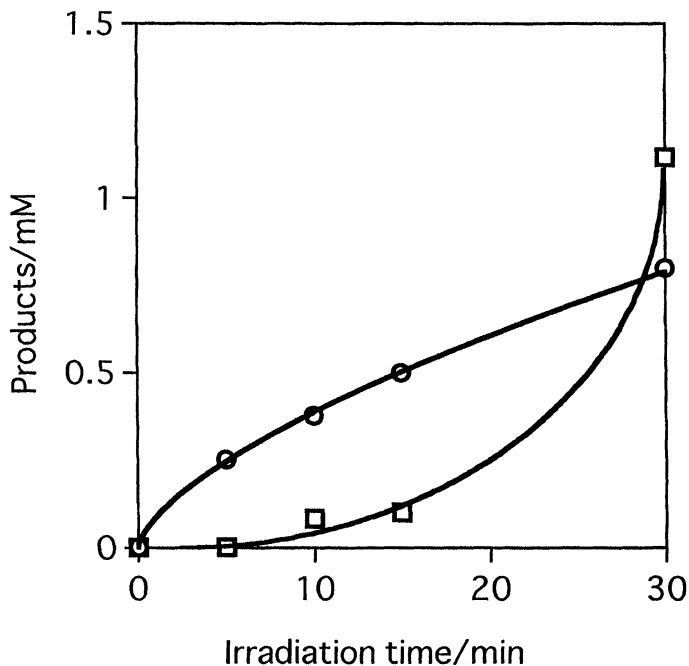


FIGURE 2 Relationship between the quantities of main products in DO with irradiation time. Aqueous 30% H₂O₂ feeding rate: 3.4 ml h⁻¹. □: GA, ○: TA, △: malic acid.

in DO by XeF-laser irradiation as a function of irradiation time at H₂O feeding rate of 3.4 ml h⁻¹. As shown, only negligible amounts of products other than GA and TA were observed even on irradiation for 45 min (pH value of the reaction mixture after 45 min was ca. 6.7). It is noteworthy that the quantity of TA increases with time up to about 30 min, and that is much greater than that of GA obtained within 25 min. The selectivity of TA formation was 76 and 73% for 10- and 15-min irradiation, respectively, in sharp contrast to 6% in H₂O. Moreover, from the comparison of Figure 1 with Figure 2, it was seen that the quantity of TA in DO is much larger than that in H₂O. Thus, it was found that TA is selectively and directly synthesized by XeF-laser irradiation of MA containing lower concentration of H₂O₂ in DO at room temperature.

The above result suggests that the polarity of solvents is an important factor for the selective formation of TA. So, in order to confirm this point, a series of experiments were carried out using mixed solvents of DO and H₂O having various compositions and polar solvents other than H₂O. As shown in Table II, the addition of DO to H₂O resulted in rapid elevation of TA selectivity which further elevated with increasing fraction of DO. Moreover, as shown in Table III, in MeOH the selectivity was almost the same as that in H₂O, in sharp contrast to DO. Similarly, neither DMF, MeCN, nor THF showed sensitization of TA selectivity compared with that in H₂O. Consequently, these results evidently indicate that the selective and efficient formation of TA is more favorable in nonpolar solvents than in polar solvents.

TABLE II Effects of DO fraction on the selectivity of TA formation by XeF-laser irradiation in DO-H₂O mixed solvents^a

<i>DO fraction vol%</i>	<i>TA selectivity mol%</i>
0	6
25	7
50	20
75	24
100	76

^a Irradiation time: 10 min, H₂O₂ feeding rate: 3.4 ml h⁻¹

TABLE III Solvent effects on the selectivity of TA formation by XeF-laser irradiation^a

<i>Solvent</i>	<i>TA selectivity mol%</i>
H ₂ O	6
DO	76
MeOH	4
DMF	3
MeCN	2
THF	3

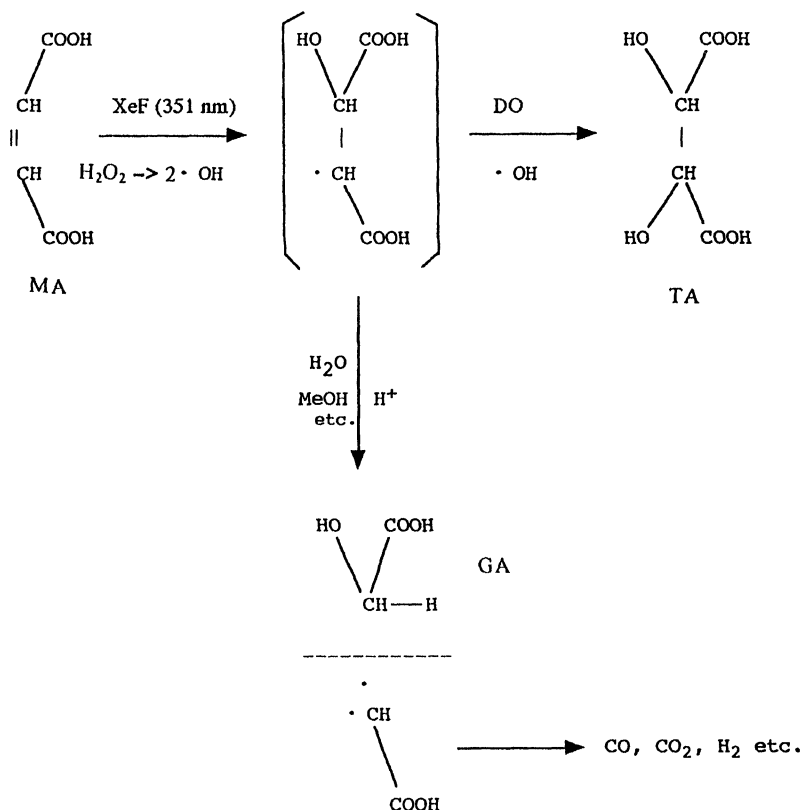
^aIrradiation time: 10 min, H₂O₂ feeding rate: 3.4 ml h⁻¹.

4. DISCUSSION

H₂O₂ showed a broad absorption band in the wavelength range (190 ~ 350 nm) shorter than 350 nm, on the other hand, the absorption band of MA was shorter than 300 nm. It can be, therefore, considered that the initiating species of TA formation in this system using laser beams ranging in wavelength from 193 to 351 nm is •OH formed efficiently by the laser-photolysis of H₂O₂ [4, 12]. In fact, in XeF-laser irradiation, the formation of TA including GA is suppressed by the addition of the thiocyanate ion which is an efficient scavenger of •OH [13]. Therefore, it is considered that TA is produced through the addition of two •OH to the double bond in MA. However, in ArF-, KrF-, and XeCl-laser irradiations, since not only H₂O₂ but also MA absorbs their beams, the reactions such as the isomerization [10] via a direct excitation process of MA would occur during the irradiation. In practice, in KrF-laser irradiation, the formation of FA is the main process, also via the two-photon absorption for XeCl-laser irradiation, as shown in Table I. Moreover, in ArF-laser irradiation, since all MA, H₂O₂, and products once formed by the irradiation absorb the beam, their laser-induced secondary photochemical reactions would also proceed during the irradiation. The results that an extremely small quantity of FA was produced and there was lack of the product selectivity compared with KrF- and XeCl-laser irradiations most probably support this consideration.

Furthermore, the results that the formation of TA competes with that of GA which is a similar hydroxylated products of MA, as shown in Figure 2, and their formations are strongly affected by the solvent

rather than the wavelength suggest that TA and GA are competitively produced through a common intermediate formed in the route to the hydroxylation of MA. It seems reasonable to consider that the monohydroxylated radical formed by the addition of one $\bullet\text{OH}$ to MA is the common intermediate to produce TA and GA competitively. On the other hand, the quantity of TA gradually decreased with increasing H_2O_2 feeding rate, the increase of H_2O_2 concentration accompanying rapid increases in the quantity of GA, suggesting the occurrence of such decomposition as bond cleavage of the intermediate by excess H_2O_2 to produce GA predominantly. It is generally known that the double bond is subject to cleavage in prolonged reaction time using excess reagent, for example H_2O_2 , in hydroxylation [14]. It may be, therefore, considered that the bond cleavage of the intermediate is caused by the protonic species such as H^+ and/or H_3O^+ resulting from H_2O_2 remaining in the system, following the formation of GA and the decomposition such as decarboxylation shown by the formations of CO, CO_2 etc. Similarly, it can be considered that the property of H_2O as a protogenic solvent, i.e., H^+ release, is responsible for the lower selectivity of TA formation in an aqueous solution. Moreover, this may be applied to the reaction in MeOH which also is a protogenic solvent. On the contrary, the selective and efficient formation of TA was achieved by the reaction in DO, an aprotic solvent [15]. This result and the fact that the addition of DO in H_2O remarkably elevates TA selectivity support the above consideration, namely, that in the presence of media such as protogenic solvents and H_2O_2 which release easily H^+ and this class, TA selectivity is lowered on account of the decomposition of the intermediate leading to the formation of TA by H^+ released from the media (Scheme 1). This reaction scheme may be also supported by the behavior of a quadrical formation of GA while that for TA formation is not quadrical, as shown in Figures 1 and 2. On the other hand, the large difference in the behavior of TA formations in DO and THF, grouped into the same ether solvents, may be mainly explained by the following data: THF is more reactive to $\bullet\text{OH}$ than DO [16] and also, much more than MeOH [17] and, consequently, this effect results in the larger decrease of the hydroxylated products in THF. Furthermore, all the reactions in polar solvents were more disadvantageous than those in nonpolar ones for the selective formation of TA. In this regard, it may be considered



that, since the main reaction of TA formation proceeds via a radical mechanism, the reaction is of greater advantage in nonpolar solvents than in polar solvents such as not only MeOH, H₂O and THF but also DMF and MeCN which are most useful in ionic reactions [18].

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