An efficient enantiomeric enrichment of tartaric acid using a highly intense circularly polarized light

Yuichi Shimizu* and Shunichi Kawanishi

Osaka Laboratory for Radiation Chemistry, Japan Atomic Energy Research Institute, Mii-minami 25-1, Neyagawa, Osaka 572, Japan

An efficient method is described for the enantiomeric enrichment of tartaric acid by irradiation with a focused circularly polarized light from an excimer laser.

Enantiomeric enrichment of racemates is of great importance in the synthesis of optically active compounds. Many methods are available to enrich racemates[1] and it is known that enrichment is possible by photochemical methods using circularly polarized light (CPL).[2] However, in studies already reported, the enantiomeric enrichments for this method were less than satisfactory (mostly, ee <3%) except in a few classes of compounds such as camphor.[3] It may be considered that the use of light sources with low intensity[4–6] and/or of mixed light of right (r)- and left (l)-CPL[4] are mainly responsible for such poor enrichments. We therefore attempted the enantiomeric enrichment of racemic tartaric acid (DL-TA) **1** with a highly intense r-CPL† from an XeF (351 nm) excimer laser.

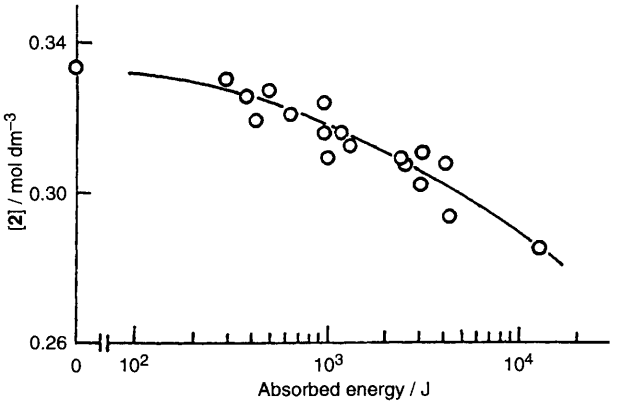


Fig. 1 The concentration of **2** in the solution of **1** (6.67×10^{-1} mol dm^{-3}) irradiated with a focused r-CPL

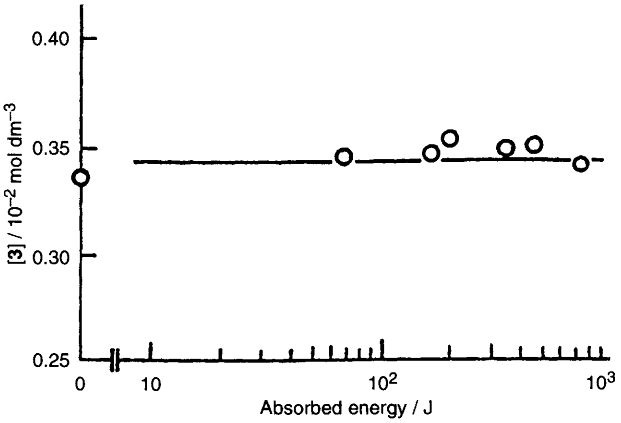
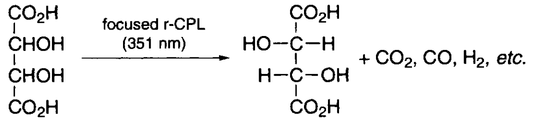


Fig. 2 The concentration of **3** in the solution of **1** (6.67×10^{-3} mol dm^{-3}) irradiated with a focused r-CPL



DL-Tartaric acid

D-Tartaric acid

Scheme 1

Fig. 1 shows the concentration of L-**2**‡ in the solution of **1** irradiated with a focused r-CPL. The concentration of **2** decreases with increasing absorbed energy. The decrease at irradiation dose of about 1×10^4 J was *ca.* 13.9% and the optical rotation§ also varied from zero before irradiation to a minus value, levorotatory, supporting the conclusion that the solution is rich in D-**3**.

On the other hand, as shown in Fig. 2, the concentration of **3**‡ remains almost constant throughout the irradiation of **1** with a focused r-CPL and did not decrease unlike **2**, Fig. 1. The optical rotation of the solution was almost zero even after irradiation with CPL of about 1×10^4 J. Also, the meso-form of TA, malic and lactic acids¶ were not produced in all cases, indicating that photoracemization did not occur in this system. However, on irradiation with a focused r-CPL, gaseous products‖ such as CO, CO_2, H_2 and O_2 *etc.* were detected, suggesting decomposition had occurred. Furthermore, the decrease of [**2**] was hardly observed on irradiation of **1** with a nonfocused r-CPL (initial fluence: 26.7 mJ cm^{-2} pulse^{-1}).

These results indicate that **3** is enriched by the selective decomposition of **2** by irradiation with focused r-CPL from an XeF laser. The ee of **3** estimated from the decrease of **2** in Fig. 1 was *ca.* 7.5% at an irradiation dose of about 1×10^4 J. This enantiomeric enrichment is much larger than that (optical purity = 0.11)[4] of irradiation with mixed CPL from a Xe lamp as continuous light of low intensity. This indicates that light intensity and the unmixed light are very important factors for the efficient enantiomeric enrichment of TA, and that efficient enrichment is favoured by higher intensity and pure CPL with r or l only. In this study, the intensity of the focused r-CPL was about 150 times larger than that of the nonfocused. Thus, it was demonstrated that an enantiomer of TA can be efficiently enriched by the irradiation with a highly intense r-CPL from XeF (351 nm) laser (Scheme 1).

It can be considered that this reaction mainly proceeds through photodecomposition such as decarboxylation as judged from the gaseous products. Since TA scarcely has adsorption** at a wavelength of >300 nm, the enantiomeric enrichment is hardly observed using nonfocused CPL irradiation. The process with focused CPL from a XeF laser is expected to proceed through the selective excitation of the carboxyl chromophore in TA by multiphoton absorption.

Footnotes

† The XeF laser beam (Lumonics Hyper EX-460, initial power: 2.6 W, frequency: 16 Hz, pulse duration: 12–15 ns, beam shape: 9×34 mm^2) was converted to r-CPL (initial power: 1.3 W at 16 Hz) by passing through a polarizer and a quarter-wave plate, and focused at the centre (initial fluence:

3.8 J cm^{-2} pulse^{-1}) of the reaction vessel (light pathlength: 50 mm) with a condenser lens (focal length: 120 cm). The irradiation with a focused r-CPL was carried out to the N_2-saturated 6.67×10^{-1} (c = 10 g/100 ml) or 6.67×10^{-3} mol dm^{-3} aqueous solution of **1** (Tokyo Kasei) at room temperature.

‡ Analysis of the irradiated solution of **1** was performed by HPLC (Shimadzu LC-6A, column: SUMICHIRAL OA-5000, column size: 4.6 × 50 mm, mobile phase: 1 mmol dm^{-3} $Cu(MeCO_2)_2$ + 0.05 mol dm^{-3} NH_4MeCO_2 in H_2O/Pr^iOH (85/15), flow rate: 1.0 ml min^{-1}, column temp.: 55 °C, detector: UV 280 nm) by referring to the authentic samples (L- and D-TA, Tokyo Kasei) in various concentrations.

§ Optical rotations were recorded on a Nihon Bunko DIP-1000 digital polarimeter.

¶ Products were analysed by ion chromatography (Yokogawa IC-100, column: SAX 1 × 2).

|| Products analyses were carried out by GC (Shimadzu GC-3BT, column: Molecular sieve 5 Å; GC-4C, column: Porapak N).

** UV-spectrum of **1** was recorded on a Shimadzu UV-2100 spectrophotometer.

References

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