Laser-induced enantiodifferentiating reaction of tartaric acid using high-intensity circularly polarized light

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High-intensity right circularly polarized light (CPL) from an XeF (351 nm) laser induces selective enrichment of D-tartaric acid (D-TA) while the left CPL induces enrichment of the L-tartaric acid (L-TA), revealing a clear correlation between enantioselection and the sense of the CPL.

As the synthesis of a racemic compound is often much easier than asymmetric synthesis, enantiomeric enrichment plays a very important role in the preparation of optically active compounds.[1] In enriching the enantiomer by photochemical means, we recently demonstrated that laser-induced synthesis of D-tartaric acid (D-TA) can be efficiently achieved by the irradiation of racemic tartaric acid (DL-TA) **1** with a highly intense right (r) circularly polarized light (CPL) from an XeF (351 nm) laser.[2] In effect, the laser-induced selective synthesis of enantiomers is a highly promising method for the development of a new field of application in the synthesis of optically active compounds, if the enantioselectivity can be controlled with CPL. Therefore, we examined the relationship between the sense of the CPL and the enantioselection by the irradiation of **1** and L-TA **2**† with r- and left (l)-CPL.‡ We describe here a new laser-induced enantiodifferentiating reaction of tartaric acid (TA) with the highly intense CPL from an XeF laser.

Initially, in order to obtain further evidence for the preferential enrichment of the D-TA **3**† by r-CPL irradiation, we attempted the irradiation of **2** with the CPL. It is noteworthy that the concentration of **2** decreases with increasing absorbed energy, as shown in Fig. 1. The decrease in this case was determined to be *ca.* 8.9% which is in excellent agreement with that (8.8%)[2] for the irradiation of **1** at *ca.* 3×10^3 J. Furthermore, the formation of **3** in **2** irradiated not only with r-CPL but also with l-CPL described later was not detectable, indicating that no photoinversion in the chirality occurs during the irradiation. Thus, it was more substantially demonstrated that the r-CPL irradiation can induce the selective enrichment of **3** in **1**.

In sharp contrast to the r-CPL irradiation, a decrease in the concentration of **3** was observed when **1** was irradiated with a CPL of the opposite sense, *i.e.*, a focused l-CPL, and that it decreased with increasing absorbed energy, as shown in Fig. 2. The decrease was determined to be *ca.* 19.6% (ee of the L-TA = 10.9%) at an irradiation dose of about 1×10^3 J. In contrast, as shown in Fig. 3, the concentration of **2** did not decrease and was almost constant throughout the irradiation of **1**. Such behaviour was also confirmed from the fact that the concentration is hardly changed by the irradiation even when **2** was used instead of **1**. Moreover, the decrease in concentration of **3** was negligible on irradiation of **1** with a non-focused l-CPL (initial fluence: 26.7 mJ cm^{-2} pulse^{-1}). Also, the respective behaviour of *meso*-TA,† malic acid, *etc.*, and gaseous product formation were the same as those[2] with r-CPL. Thus, it was demonstrated that the l-CPL irradiation can induce the selective enrichment of **2** in **1** in which **3** is selectively decomposed and disappears, leading to

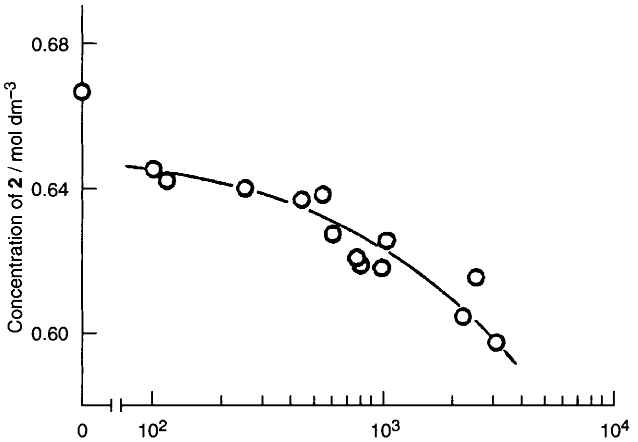


Fig. 1 The concentration of a solution of **2** (6.67×10^{-1} mol dm^{-3}) irridiated with a focused *r*-CPL

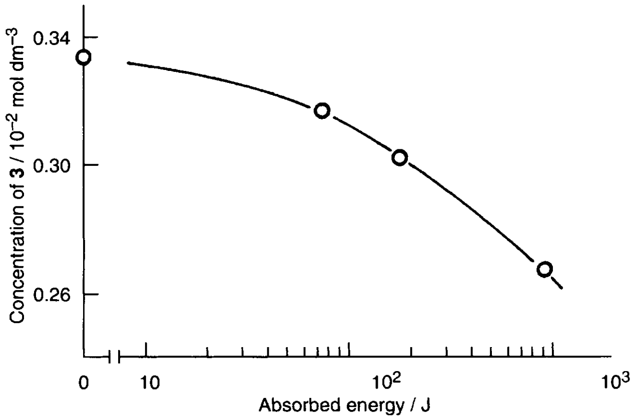


Fig. 2 The concentration of **3** in a solution of **1** (6.67×10^{-3} mol dm^{-3}) irradiated with a focused *l*-CPL

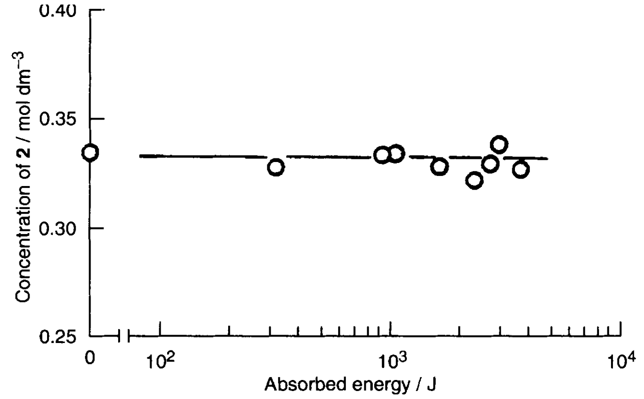
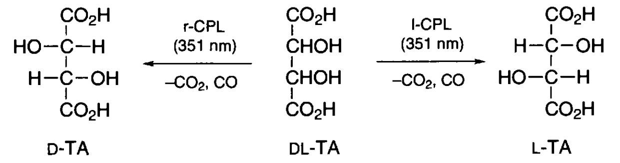


Fig. 3 The concentration of **2** in a solution of **1** (6.67×10^{-1} mol dm^{-3}) irradiated with a focused *l*-CPL

the formation of gases, and responsible for the enantioselectivity which is completely opposite to that with r-CPL. As can be seen, the switching of the sense of rotation of the plane of polarization in CPL causes an inversion in the enantioselection.

From these results, it can be concluded that high-intensity CPL irradiation can induce the enantiodifferentiating reaction of racemic tartaric acid through the selective photodecomposition of the other enantiomer with high enantioselectivity and excellent enantiocontrol only by switching the sense of the CPL (Scheme 1). It is postulated that this enantiodifferentiating reaction using the CPL from an XeF laser proceeds *via* a multiphoton absorption process, similar to that with r-CPL reported previously.[2]



Scheme 1

Footnotes

† Analyses of optically active and *meso*-TA by HPLC were carried out with a SUMICHIRAL OA-5000 column (5 cm × 4.6 mm i.d., Sumitomo Chemical Co.) as previously described.[2]

‡ The generation of r-CPL from an XeF laser was essentially similar to that described previously, that is, the r-CPL was generated by passage of the linearly polarized beam, which was obtained using a polarimeter, through an appropriately oriented (+45° to the plane of the incident) quarter-wave plate mounted in a rotatable stage. The l-CPL was obtained by switching the sense of the r-CPL by rotation of the quarter-wave plate through 90°. Both r- and l-CPL (initial power: 1.3 W at 16 Hz) were focused at the centre (initial fluence: 3.8 J $\mathrm{cm^{-2}}$ $\mathrm{pulse^{-1}}$) of the reaction vessel (light pathlength: 50 mm) with a condenser lens (focal length: 120 cm). The irradiations with the focused r- and l-CPL were carried out on the N_2-saturated 6.67×10^{-1} (c = 10 g/100 ml) and/or 10^{-2}, 10^{-3} mol $\mathrm{dm^{-3}}$ aqueous solutions of **1** and **2** at room temp.

References

1 For example, see K. Saigo, in *Kogaku Kasseitai*, ed. H. Nohira, Asakura Shoten, Tokyo, 1989, ch. 2; Y. Inoue, *Chem. Rev.*, 1992, **92**, 741.

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