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Absolute Asymmetric Photoreactions of Aliphatic Amino Acids by Circularly Polarized Synchrotron Radiation: Critically pH-Dependent Photobehavior

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Abstract: The absolute asymmetric photoreaction (AAP) of racemic aliphatic amino acids, such as alanine (Ala) and leucine (Leu), by left- and right-handed circularly polarized light (*l*- and *r*-CPL) irradiation was investigated in aqueous solutions at various pHs, by using the Onuki-type polarizing undulator installed in an electron storage ring. The magnitude of the optical purity (op) generated and the enantiomer-enriching mechanism operative in the AAP were found to be entirely dependent on the ionic state (and thus pH) of the amino/carboxylic acid moieties. At pH 1, the op of Ala and Leu determined by circular dichroism (CD) spectral measurement gradually developed with CPL irradiation, according to Kagan's equation. In contrast, irradiation at pH 7 gave op's much smaller than the theoretical values predicted by Kagan's equation. However, it turned out that the photodecomposition at pH 7 produces the corresponding α-hydroxycarboxylic acids stereoselectively, the CD sign of which is just opposite to that of the remaining amino acid, thus affording the apparently small op. It is concluded that, irrespective of solution pH, the AAP of amino acid proceeds upon CPL irradiation. At pH 1, the photodecomposition of valine, Leu, and isoleucine occurs via a Norrish type II mechanism, which is also applicable to other amino acids possessing a γ-hydrogen. In the case of amino acids lacking a γ-hydrogen, such as glycine and Ala, the photodecomposition mechanism is a photodeamination/hydroxylation and a Norrish type I reaction. At pH 7, the main photoproducts were ammonia and α-hydroxycarboxylic acids that were produced via photodeamination.

Introduction

A variety of biotic and prebiotic theories have been proposed to explain the origin of homochirality in biomolecules, and a number of potential mechanisms have been experimentally examined.[1−7] One of the most studied hypotheses is that irradiation by circularly polarized light (CPL) results in the enantiomeric enrichment of amino acids;[8−10] the photochemistry involved in such processes is enantiomer-selective photodestruction with CPL,[11] which may be called "absolute asymmetric synthesis"[12−14] or "absolute asymmetric photoreaction" (AAP). However, the exact origin and type of CPL that may have brought about such AAP is still unclear.[1,2] Recently, it was reported that some of the amino acids found within the Murchison meteorite, a number of which were unnatural amino acids and therefore could not have arisen from terrestrial contamination, were enantiomerically enriched.[15−18] A result of this and other similar discoveries is that a significant degree of interest is currently been paid to the idea that the enantiomeric enrichment of amino acids by CPL irradiation proceeded in outer space.[8,19,20]

It is a principle of AAP with CPL that the relative differences in the molecular absorption coefficients of an optically pure compound toward left- and right-handed circularly polarized light (*l*- and *r*-CPL), at the excited wavelength, result in different photoreaction rates for each enantiomer. The degree of preferential excitation is determined by the anisotropy factor (*g* factor),

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which is defined as the normalized difference in molecular absorption coefficients between optical isomers toward *l*- and *r*-CPL at a given wavelength:

$$g = |\epsilon_l - \epsilon_r|/\epsilon = \Delta\epsilon/\epsilon$$

where $\epsilon = (\epsilon_l + \epsilon_r)/2$ and $0 \leq g < 2$.[9,12,14,21−23] It has been reported that enantiomeric enrichment of some amino acids can be experimentally obtained by CPL irradiation.[24−26] However, a detailed understanding of the reaction mechanism operating in the AAP of amino acids has yet to be achieved. In our recent paper,[24] we reported the pH dependency of the obtained optical purity (op) of racemic leucine (*rac*-Leu) upon irradiation by *l*- and *r*-CPL. The CPL is generated by a polarizing undulator installed in an electron storage ring, NIJI II; this is the most suitable CPL source for the UV and VUV regions.[9,27] The AAP of aliphatic amino acids having a γ-hydrogen, such as Leu, proceeds via γ-hydrogen abstraction by the ester carbonyl group (Norrish type II mechanism) in acidic solution, while at neutral or alkaline pHs, no op is observed.[24] At that time, the photodecomposition products required to explain the details of photodecomposition of aliphatic amino acids at pHs 7 and 11 had not be identified. We speculated that some and/or all parts of decomposition of Leu at pHs 7 and 11 proceeded via achiral thermal process(es) and/or via indirect photochemical process(es). However, irrespective of the solution pH, if a *g* factor exists and the reaction proceeds via the excited state (governed by the *g* factor), AAP with CPL should occur. Consequently, we have undertaken to identify the photodecomposition products with the aim to clarify the detailed nature of the mechanism occurring at pH 7.

Since the early part of the past century, several photodecomposition mechanisms have been proposed, but the correct pathway(s) have yet to be unambiguously determined.[28,29] It has been thought that photodeamination is the main mechanism in the case of various amino acids.[28−32] It has been reported that NH_3 and glycolic acid (**1h**) are photoproducts of glycine (Gly), and NH_3 and lactic acid (**2h**) are photoproducts of alanine.[28,29,31−35] However, methane, carbon dioxide, and other small molecules have also been reported as photodecomposition products.[28] In the cases of Val, Leu, and Ile, NH_3 has been detected, but other, as-yet unidentified and unexplained products have also been detected. Hence, it would be premature to say that the photodecomposition mechanism of amino acids has been clarified in detail.[24,28,29]

In this comprehensive study on the photoreactions of aliphatic amino acids such as glycine (Gly), alanine (Ala), valine (Val), leucine (Leu), and isoleucine (Ile), we have identified all major photoproducts, determined their yields, and clarified the photodecomposition mechanisms at acidic and neutral pHs. On this basis, we elucidate the relationship between the process resulting in enantiomeric enrichment by CPL irradiation (AAP) and the photodecomposition mechanism. Consequently, this report aims to contribute to the understanding of the photochemistry of amino acids and also to give insight into how the origin of homochirality in biomolecules may have occurred by CPL irradiation.

Experimental Section

Materials. Gly (**1**, Wako), *rac*-Ala (**2**, Wako), *rac*-Val (**3**, Wako), *rac*-Leu (**4**, Wako), *rac*-Ile (**5**, Wako), D-Ala (Wako), L-Ala (Wako), D-Leu (Wako), L-Leu (Wako), *rac*-aspartic acid (Wako), *rac*-threonine (Wako), *rac*-serine (Wako), *rac*-glutamic acid (Wako), *rac*-lysine (Aldrich), *rac*-histidine (Aldrich), *rac*-arginine (Wako), ammonia (Wako), methylamine (**1a**, Wako), ethylamine (**2a**, Wako), isobutylamine (**3a**, Aldrich), isoamylamine (**4a**, Aldrich), 2-methylbutylamine (**5a**, Aldrich), formic acid (Wako), acetic acid (**1c**, Wako), propionic acid (**2c**, Wako), isovaleric acid (**3c**, Aldrich), 4-methylvaleric acid (**4c**, Aldrich), 3-methylvaleric acid (**5c**, Aldrich), isobutyric acid (Wako), 2-methylbutyric acid (Wako), 2-chloropropionic acid (Aldrich), acrylic acid (**1e**, Aldrich), 3,3-dimethylacrylic acid (**3e**, Aldrich), 4-methyl-2-pentenoic acid (**4e**, TCI), glycolic acid (**1h**, Aldrich), lactic acid (**2h**, Aldrich), 2-hydroxy-3-methylbutyric acid (**3h**, Aldrich), 2-hydroxyisocaproic acid (**4h**, Aldrich), pyruvic acid (**2k**, Aldrich), 2-oxo-4-methylvaleric acid (**4k**, Pfaltz & Bauer), (*S*)-*sec*-butylamine (Aldrich), (*S*)-2-methylbutyric acid (Aldrich), (*R*)-lactic acid solution (*R*-**2h**, Aldrich), (*S*)-lactic acid solution (*S*-**2h**, Aldrich), (*S*)-2-hydroxyisocaproic acid (*S*-**4h**, Aldrich), isoamyl alcohol (Wako), isobutanol (Wako), isobutyraldehyde (Aldrich), 2-methylbutyraldehyde (TCI), 2-methylpropene (Aldrich), and 2,2,3,3-tetramethylbutane (TCI) were used as received. In this paper, amino acids are numbered sequentially as R-CH-(NH_2)COOH, **1** (R = H); **2** (R = CH_3); **3** (R = *i*-Pr); **4** (R = *i*-Bu); **5** (R = *sec*-Bu), while the relevant carboxylic acids, hydroxycarboxylic acids, and ketocarboxylic acids derived therefrom are identified by suffixes **a**, **h**, and **k**, respectively.

In most cases, the acidic solutions of amino acids were prepared with 0.1 or 0.01 M standard HCl solution, the alkaline solutions were prepared with 0.1 M standard NaOH solution, and the neutral solutions (pH 7) was prepared with distilled water. The solutions of **4a** and *S*-**4h** were prepared with 1 M standard HCl solution, 0.1 M standard HCl solution, distilled water, and 1 M standard NaOH solution. For CPL and linearly polarized light (LPL) irradiation, the concentrations of amino acids were adjusted to be 5.01−5.78 mM, except for Ala solutions for CPL irradiation (11.6 mM) and Gly (11.7−12.7 mM). The pH of the solutions was measured using Horiba pH meter F-12 at 24.2−24.5 °C. The measured pHs deviated only slightly from the formal values indicated in the text: Leu, pH 1 = 1.00, pH 2 = 2.00, pH 3 = 3.02, pH 7 = 6.74, pH 11 = 10.92; Ala, pH 1 = 1.00, pH 2 = 2.01, pH 3 = 3.01, pH 7 = 6.76, pH 11 = 10.91; Gly, pH 1 = 1.01, pH 7 = 6.89; Val, pH 1 = 1.03, pH 7 = 6.91; Ile, pH 1 = 1.03, pH 7 = 6.90.

Photolysis. Each solution (2 mL) of amino acid was melt-sealed in a rectangular quartz cell (1 cm × 1 cm × 4 cm) under an argon atmosphere (for volatile product analysis, the rectangular quartz cell was capped with a Teflon/silicon rubber stopper) and was irradiated with the CPL and LPL generated with the Onuki-type polarizing undulator installed in the electron storage ring NIJI II at the Metrology Institute (former name, Electrotechnical Laboratory).[27]

Analysis. The circular dichroism (CD) spectra were measured using JASCO 720 WI and 725 CD spectrometers. The UV spectra were

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measured using a JASCO V-560 spectrometer. The photolyzed solutions were analyzed using a 725 CD spectrometer with a drum cell ($\phi = 13$ mm, light path length = 5 mm) at 23 ± 1 °C.

The amino acids in the solutions before and after photoirradiation were analyzed and estimated by amino acid analysis of the reaction that utilized ninhydrin, using a Hitachi L-8500 HPLC with a Hitachi 2650L column (80 mm × 4.6 mm i.d.). For the identification of Gly, the photolyzed solution was also analyzed by HPLC using a Hitachi LaChrom with a Sumichiral OA-5000 column (150 mm × 4.6 mm i.d.) (mobile phase, 2 mM $CuSO_4$, water/isopropanol = 100/0.1) and by capillary electrophoresis using G1600A (Agilent Technologies) with a G1600-64211 column (1040 mm × 50 μm i.d.) (Agilent Technologies basic anion buffer). The amines in the photolyzed solutions were analyzed by ion chromatography using a Dionex DX-500 with a Dionex CG10 (50 mm × 4 mm i.d.)/CS10 column (250 mm × 4 mm i.d.) (mobile phase, 30 mM methanesulfonic acid; removal phase, 40 mM tetramethylammonium hydroxide) for NH_3, **1a**, and **2a**, and a Dionex DX-500 with a Dionex CG14 (50 mm × 4 mm i.d.)/CS14 column (250 mm × 4 mm i.d.) (mobile phase, 30 mM methanesulfonic acid and 5% acetonitrile; removal phase, 40 mM tetramethylammonium hydroxide) for **3a**−**5a**. The carboxylic acids in the photolyzed solutions were analyzed by ion chromatography using a Dionex 2000i with an ICE AS6 column (250 mm × 9 mm i.d.) (mobile phase, 0.4 mM 1-octanesulfonic acid; removal phase, 5 mM tetra-*n*-butylammonium hydroxide) for HCOOH, **1c**, **1h** and **2h**, a Dionex 2000i with an ICE AS1 column (250 mm × 9 mm i.d.) (mobile phase, 0.5 mM 1-octanesulfonic acid; removal phase, 5 mM tetra-*n*-butylammonium hydroxide) for **2c**−**4e** and **3h**−**4k**, and a Dionex 2000i with an ICE AS1 column (250 mm × 9 mm i.d.) (mobile phase, 1 mM 1-octanesulfonic acid; removal phase, 5 mM tetra-*n*-butylammonium hydroxide) for **1c** and 2-methylbutyric acid. The carboxylic acids in the photolyzed solutions were also analyzed by capillary electrophoresis using G1600A (Agilent Technologies) with a G1600−64211 column (1040 mm × 50 μm i.d.) (Agilent Technologies basic anion buffer). *R*-**2h**, *S*-**2h**, *R*-**4h**, and *S*-**4h** in the photolyzed solutions of L-Leu and L-Ala were also analyzed by HPLC using Gulliver (JASCO) with a Sumichiral OA-6100 (150 mm × 4.6 mm i.d.) column for analysis of photoracemization of L-Ala and L-Leu (mobile phase, for L-Ala, 1 mM $CuSO_4$ solution, for L-Leu, 2 mM $CuSO_4$ solution/acetonitrile = 90/10). Half a milliliter of vapor gas was collected from the vapor phase with a gas-sampling syringe, and the volatile products from the photolyzed solutions were analyzed by GC−MS using a Hewlett-Packard HP-6890 GC/HP-5973 MSD with a J&W DB-wax column (30 mm × 0.25 mm i.d.). The amount of each product was estimated by using isobutanol (or 2,2,4-trimethylpentane) for the standard compound.

Isoamyl alcohol in aqueous **4a** solution irradiated at 215 nm by LPL (pH 1 and pH 7) was analyzed by GC using a Shimadzu GC-17A with a J&W DB-wax (30 m × 0.53 mm i.d.) column which was equipped with Shimadzu autoinjector AOC-20I.

Results and Discussion

pH Dependence of Chiroptical Properties. To determine the wavelength that gives the highest *g* factor, the UV and CD spectra of aliphatic amino acids were measured under the conditions employed in the absolute asymmetric photoreaction (AAP) experiments. Figure 1a,c,e shows the chiroptical properties of D- and L-Leu at various pHs. The UV and CD spectra change on varying the solution pH and are in agreement with those reported in the literature.[36−38] These spectral changes correspond to the compositional changes of different ionic states of Leu in accordance with the changes in the solution pH. At pH 1, the form of the carboxyl group of Leu is a carboxylic acid, and that of the amino group is an ammonium group. The UV and CD bands at 208 nm arise from the n,π^* transition of the carboxyl group. In accordance with the pH change from 1 to 7, the form of the carboxyl group changes from carboxylic acid to carboxylate anion. In Figure 1a,c, it is observed that the UV and CD band shifts to <200 nm respectively, and an isosbestic point is observed in the UV and CD spectra as the pH changes from 1 to 7 (UV 209 nm, CD 201 nm). These spectral changes reflect the different forms of the carboxyl group at pHs 1 and 7. At pH 11, Leu exists as an aminocarboxylate anion. The amino group contributes to the UV and CD bands, especially the band at 230 nm, which is assigned to the n,σ^* transition.[36,38] Figure 1e shows the *g* factors of D- and L-Leu at various pHs. The compositional change of Leu with the solution pH is reflected in the *g* factor spectra. The amino group also contributes to the *g* factor on changing the solution pH from 7 to 11. Figure 1e suggests that the *g* factor at pH 11 is comprised of the n,π^* transition of the carboxylate group and the n,σ^* transition of amino group, as the *g* factor shows two peaks at <205 and 230 nm. It is observed that the g_{215} (*g* factor at 215 nm) is large (beyond 0.01) over the range of pH 1−11; thus, this wavelength was chosen for the irradiation of the Leu solutions at 215 nm.

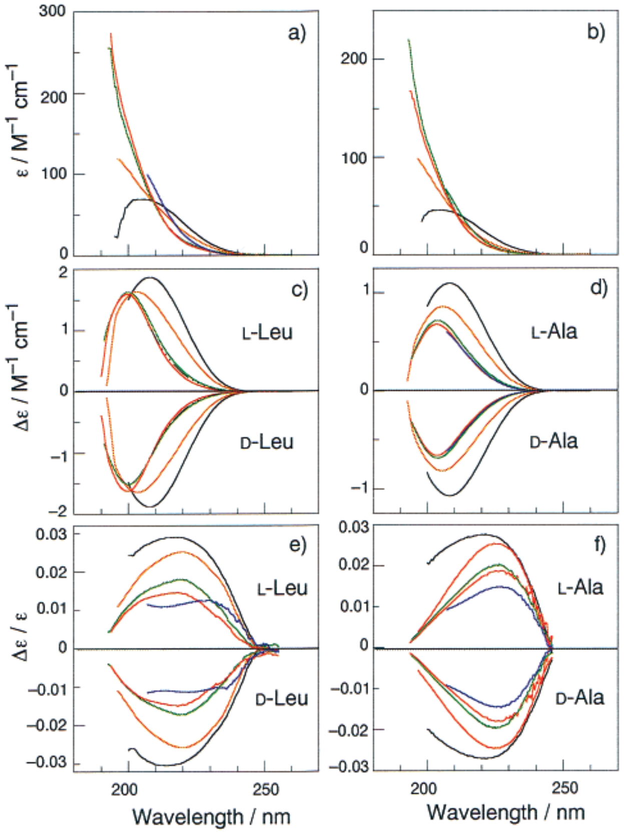

Figure 1. UV (a,b) and CD (c,d) spectra and *g* factors (e,f) of D- and L-Leu (left) and D- and L-Ala (right) at pHs 1 (black line), 2 (orange line), 3 (green line), 7 (red line), and 11 (blue line).

In the cases of D- and L-Ala, the molecular structures and excited states are very similar to those of D- and L-Leu. Accordingly, the changes of the UV and CD spectra (Figure 1b,d) with the pH changes are very similar to those in D- and L-Leu, with an isosbestic point in the UV spectrum at 210.5

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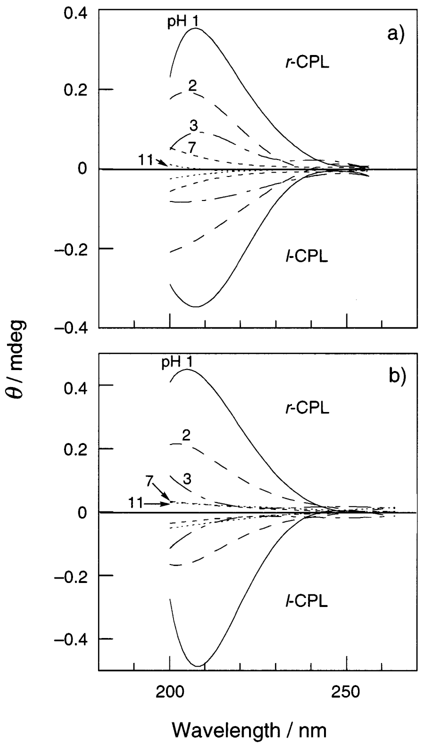

Figure 2. CD spectra of aqueous Leu (a) and Ala (b) solutions irradiated at pHs 1 (largest θ), 2, 3, 7, and 11 (smallest θ); irradiation wavelength, 215 nm; initial concentration, [*rac*-Leu] = 5.01 mM, [*rac*-Ala] = 11.6 mM; dose, 60 mA h for Leu, 100 mA h for Ala. % Decomposition: for Leu, pH 1 = 15.4−14.7 pH 2 = 14.7−12.3, pH 3 = 9.9−9.8, pH 7 = 7.5−6.5, pH 11 = 7.3−5.9; for Ala, pH 1 = 24.3−23.6 pH 2 = 16.6−14.8, pH 3 = 10.1−9.7, pH 7 = 8.0−7.4, pH 11 = 8.7−8.2.

nm.[36,37,39] The composition changes of D- and L-Ala with the solution pH also reflect the changes in the *g* factor spectra (Figure 1f). The main group contributing to the *g* factor of D- and L-Ala is also thought to shift from the carboxyl group to the amino group on changing the solution pH from 7 to 11.

pH Dependence of the Enantiomeric Enrichment upon CPL Irradiation. (a) CD Spectral Changes of *rac*-Leu and Ala Irradiated with CPL at Various pHs. The g_{215} was beyond 0.01 over the pH range 1−11. Consequently, this wavelength (215 nm) was chosen for the irradiation of the amino acid solutions by CPL. Figure 2a,b shows the final CD spectra of *rac*-Leu and *rac*-Ala solutions irradiated at 215 nm with CPL at various pHs.

When Leu was irradiated at pH 1, the CD spectra showed λ_{max} at 208 nm. The profile of the CD spectra at pHs 1 and 2 corresponded well with the molar CD spectra of enantiopure Leu, as shown in Figure 1c. For *r*-CPL irradiation, the resultant sign of the CD spectra was positive, and for *l*-CPL irradiation, the sign was negative. The signs and shapes of the observed CD mean the preferential excitation and photodecomposition; e.g., the preferential excitation and decomposition of D-Leu occur by *r*-CPL irradiation, with an enantiomeric enrichment of L-Leu resulting. In sharp contrast, the CD intensities at 215 nm of the Leu solutions irradiated at pHs 7 and 11 were practically zero, even after the dose attained to 200 mA h and ca. 18% of Leu was decomposed.

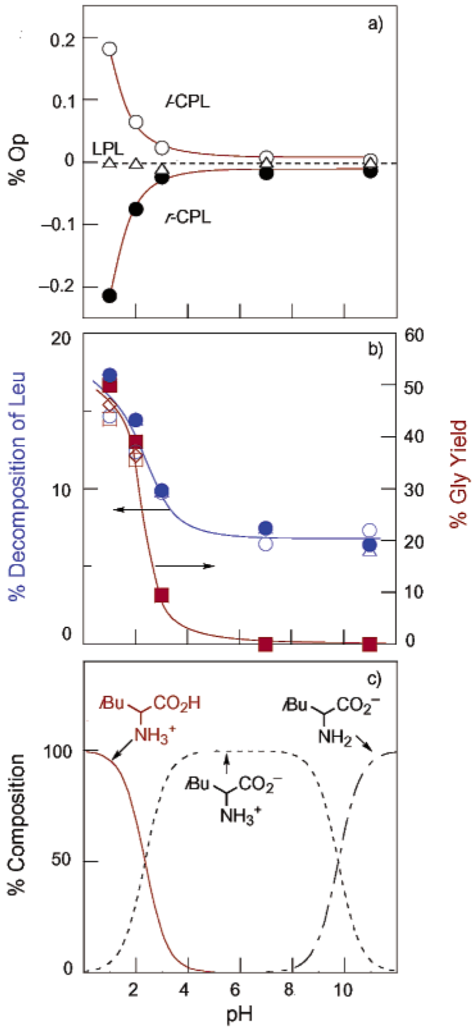

Figure 3. (a) % op of Leu (determined by CD measurement), (b) % decomposition of Leu and % Gly yield (based on consumed Leu) upon irradiation by *l*-CPL (○,□), *r*-CPL (●,■), and LPL (△,◇) at 215 nm, and (c) % composition of each ionic species of Leu, as a function of solution pH. Dose: 60 mA h in all runs performed at pHs 1−11.

In the case of Ala irradiated at 215 nm by CPL at various pHs, the CD spectral changes were very similar to those of Leu. Again, the CD intensities of the solutions irradiated at pH 7 and 11 were zero.

(b) pH Dependence of the op and Conversion. Figure 3a shows the pH dependence of the % op of Leu. Each op was estimated using the equation (op of Leu) = $\{\theta_{215}/33(\Delta\epsilon_{215}$ of D- or L-Leu)}/[Leu], where θ_{215} is the ellipticity at 215 nm. The sign of op is defined as the sign of Leu = {[D-Leu] − [L-Leu]}/{[D-Leu] + [L-Leu]},[24] with the [Leu] estimated by amino acid analysis. As the solution pH changes from 1 to 11, the % op of Leu became smaller than that predicted by applying Kagan's theoretical approach, becoming almost zero at pHs 7 and 11. Kagan's theoretical equation describes the relationship between the enantiomeric enrichment (ee) and the conversion, with the *g* factor at a specific irradiation wavelength.[9,12,21,40] In the present case, we define the op as corresponding to the ee, because it is impossible to determine small ee's (<0.5%) using GC or HPLC. Leu was decomposed by photoirradiation at 215

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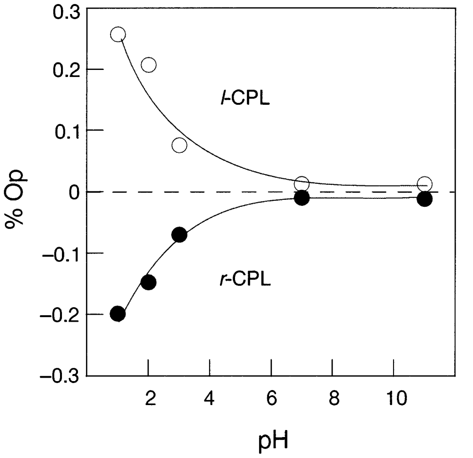

Figure 4. pH dependences of the % op of Ala (determined by CD measurement) upon irradiation by *l*-CPL (○) and *r*-CPL (●) at 215 nm. Dose: 100 mA h at pHs 1−11.

nm over the range pH 1−11. According to the calculation using Kagan's equation, the % op should be nearly 0.1% at pH 7;[24] however, the observed op was significantly smaller than that predicted by the measured *g* factor (Figure 1e) and conversion (decomposition) (Figure 3a).

The pH dependence of the op of Ala is the same as that for Leu, obtained by the same procedures as for Leu (Figure 4). It is noted that, in comparison to that at pH 1, the degree of photodecomposition became smaller as the solution pH changed from 1 to 11.

There are a number of possible rationales for why the op of CPL-irradiated Ala and Leu is pH-dependent: (1) Thermal racemization at pH 7−11. It is known that amino acids thermally racemize under alkaline condition.[39] The rate is dependent on pH and temperature. (2) Photoracemization. At pH 1, photoracemization does not proceed because the relationship between the op and conversion obeys Kagan's equation. At pH 4 and above, the carboxylic moiety of amino acid becomes a carboxylate ion, photoexcitation of which would lead to racemization, possibly through deprotonation/protonation of the α-proton. In such a case, the observed op may be smaller than that expected from ideal asymmetric photodestruction but not equal to zero, unless random energy migration among substrate molecules takes place. (3) Diminishing the op by the chiral photoproduct. At pH 1, chiral photoproducts which can cancel out the CD arising from the AAP of Leu are not produced. At pH 7, chiral photoproducts are produced and may result in apparent diminishing of the op from the AAP of Leu.

However, the CD intensities of the solutions of L-Leu and D-Ala at pH 11 were found to have slightly decreased (ca. 5%) when the solutions were left at room temperature for a week, but the UV spectra remained unchanged.[41] Thus, the rate of thermal racemization is very slow, and therefore it is unlikely that thermal racemization is responsible for the zero op of Leu and Ala after CPL irradiation at 215 nm at pH 7−11. The second possibility, i.e., photoracemization, is also less plausible, since such photoreaction has not been reported to occur with L-Ala.[29] Our own examinations revealed that LPL irradiations of L-Ala and L-Leu under comparable conditions afford the corresponding D-isomer in only 1.5−2.0% yield (based on total decomposition), as shown in Figure 5. Hence, the photoracemization cannot rationalize the zero op obtained upon CPL irradiation at pH 7.

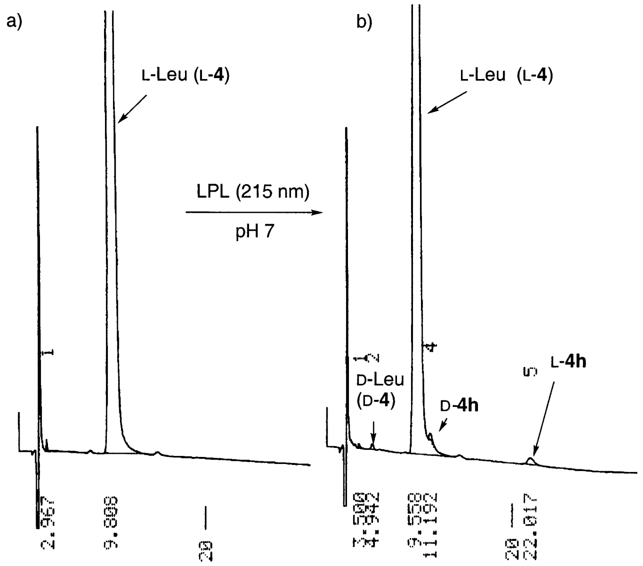

Figure 5. HPLC analysis of L-Leu (5.3 mM) irradiated at 215 nm (pH 7) with LPL (a) before irradiation and (b) after irradiation; dose, 200 mA h; % decomposition of L-Leu, 11.3%; yield of **4h**, 49.5% (based on the consumed L-Leu). Analysis: chiral column, Sumichiral OA-6100 (150 mm × 4.6 mm i.d.); mobile phase, aqueous $CuSO_4$ (2 mM)/acetonitrile = 90/10; flow rate, 1.0 mL/min; column pressure, 60 kg/cm^2; injection, 10 μL; detection, 254 nm; attenuation, 64 mV/full scale.

pH Dependence of Photodecomposition Mechanism: Photodecomposition Products. Table 1 and Scheme 1 show the result of product analysis of a series of aliphatic amino acids, i.e., Gly (**1**), Ala (**2**), Val (**3**), Leu (**4**), and Ile (**5**), irradiated by the LPL at pHs 1 and 7. NH_3, HCOOH, and acetic acid (**1c**) were detected as common photoproducts. Also detected were amines (**1a**−**5a**) and α-hydroxycarboxylic acids (**1h**−**4h**), with the corresponding structures derived from the substrate amino acids. Other miscellaneous products include propionic acid (**2c**) and isobutyric acid obtained upon photolysis of Ala (and Ile) and Val, respectively. In the literature,[29,33] Ala photochemically decomposes, producing NH_3, glycolic acid (**1h**), and pyruvic acid (**2k**) in 0.01 M HCl solution. However, irrespective of solution pH, ketocarboxylic acids (**2k** and 2-oxo-4-methylvaleric acid **4k**) were not detected by ion chromatography and capillary electrophoresis as photoproducts of Ala and Leu.

Only at pH 1, Gly was detected as the main product in the cases of Val, Leu, and Ile,[24] with the yield of Gly going up to approximately 50% of the total photodecomposition products. Significantly, it was reported that Ala photochemically produces Gly,[34] but Gly was not detected in this study by any method of analysis.

For amine derivatives, irrespective of the solution pH and the kind of amino acid, NH_3 was detected; this is in agreement with results reported previously.[29,34] The yield of NH_3 for each amino acid at pH 7 was much larger than that at pH 1. Amines **3a**−**5a**, produced upon photolyses of Val, Leu, and Ile, were produced in low yields (0−6%). In the cases of Gly and Ala, irrespective of solution pH, the relevant amines **1a** and **2a** were detected in larger quantities (5−15% yield).

For carboxylic acid derivatives, irrespective of the solution pH and the kind of amino acid, HCOOH, acetic acid **1c**, and

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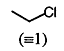
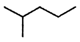
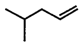
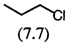
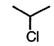
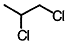
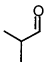
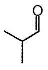
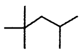
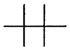
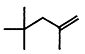
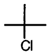
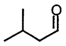
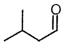
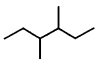
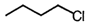
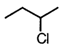
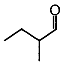
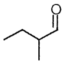
[41] See Supporting Information.

Table 1. Nonvolatile Products Detected in Aqueous Solutions of Aliphatic Amino Acids $RCH(NH_2)CO_2H$ (**1**−**5**) Irradiated by Linearly Polarized Light at 200 and/or 215 nm[a]

						% yield[b]						
amino acid	pH	irradiation wavelength/nm	concn/mM	absorbance	% decomp	Gly (**1**)	NH_3	RCH_2NH_2 (**Xa**)	HCO_2H	CH_3CO_2H (**1c**)	$CH_3CH_2CO_2H$ (**2c**)	RCH(OH)CO_2H (**Xh**)
Gly (**1**)	1	215	12.7	0.27	3.9		20.5	7.7 (**1a**)	11.3	22.3		46.2 (**1h**)
	7	215	12.3	0.19	4.9		32.7	6.1 (**1a**)	*c*	0.8		34.9 (**1h**)
Ala (**2**)	1	215	5.7	0.21	14.5	*c*	35.2	15.2 (**2a**)	4.5	8.5	2.5	11.8 (**2h**)
	7	215	5.4	0.13	3.8	*c*	57.9	5.3 (**2a**)	6.3	17.1	1.6	36.8 (**2h**)
Val (**3**)	1	215	5.7	0.30	22.8	54.4	11.0	c	1.8	5.0	*c*	*c*
	7	215	5.6	0.18	6.4	*c*	35.9	1.6 (**3a**)	4.8	2.8	*c*	16.1 (**3h**)
Leu (**4**)	1	200	5.3	0.33	16.9	48.8	*d*	*d*	*d*	*d*	*d*	*d*
		215	5.2	0.29	17.4	46.0	14.9	c	2.9	25.7	*c*	*c*
	7	200	5.3	0.84	9.5	*c*	70.5	7.4 (**4a**)	1.4	1.1	*c*	37.5 (**4h**)
		215	5.2	0.17	8.1	*c*	42.0	2.5 (**4a**)	4.1	9.9	*c*	13.3 (**4h**)
Ile (**5**)	1	215	5.4	0.29	22.8	51.8	9.2	*c*	1.9	28.4	*c*	*d*
	7	215	5.6	0.18	3.3	*c*	87.9	6.1 (**5a**)	8.2	9.2	*c*	*d*

[a] See Table 2 for volatile products. Dose: 60−61 mA h at pH 1; 80−81 mA h at pH 7. [b] Product yield based on consumed amino acid. [c] Yield <1%. [d] Not determined.

Table 2. Volatile Products from Aliphatic Amino Acids $RCH(NH_2)CO_2H$ (**1**−**5**) upon Irradiation with Linearly Polarized Light at 215 nm[a]

amino acid	pH	% decom-position	relative product ratio			
			alkane	alkene	alkyl chloride	aldehyde
Gly (**1**)	1	3.9	*b*	*b*	*c*	*c*
	7	4.9	*b*	*b*	*c*	*c*
Ala (**2**)	1	14.5	*b*	*b*	 (≡1)	 (1)
	7	3.8	*b*	*b*	*c*	 (1)
Val (**3**)	1	22.8	 (1.3)	 (4.3)	 (7.7)  (8.7)  (≡1)	 (<0.1)
	7	6.4	*c*	*c*	*c*	 (1.1)
Leu (**4**)	1	17.4	 (0.8)  (1.9)	 (1.4)  (< 0.1)	 (≡1)	 (0.5)
	7	8.1	*c*	*c*	*c*	 (1)
Ile (**5**)	1	22.8	 (1.5)	 (< 0.1)	 (≡1)  (2.5)	 (<0.1)
	7	3.3	*c*	*c*	*c*	 (0.5)

[a] Gaseous samples, taken by a gastight syringe from the same samples as in Table 1, were analyzed by GC. [b] Not determined. [c] Formation not detected.

α-hydroxycarboxylic acids **1h**−**4h**, in which each amino group was replaced by a hydroxyl group, were detected. At pH 7, hydroxycarboxylic acids were the main photoproducts, and, except for Gly, the yields at pH 1 were negligible or considerably less than those at pH 7. Propionic acid **2c** was detected at either pH in the case of Ala. At pH 7, it was confirmed by ion chromatography and capillary electrophoresis that alkenoic acids such as acrylic acid **2e**, 3,3-dimethylacrylic acid **3e**, and 4-methyl-2-pentanoic acid **4e** were not produced.

Furthermore, the volatile products of Gly, Ala, Val, Leu, and Ile irradiated by LPL (215 nm) were qualitatively analyzed. Table 2 shows the results obtained by GC−MS at pH 1 and pH 7, respectively. At pH 1, alkanes, alkenes, alkyl chlorides, and small amounts of aldehydes were detected, while at pH 7 aldehydes were detected.[29,32]

pH Dependence of Absolute Asymmetric Photoreaction: Photodecomposition Mechanism. As the main product at pH 1, Gly was produced for Val, Leu, and Ile, while at pH 7 NH_3, acetic acid 1c and hydroxycarboxylic acids were produced at the expense of Gly and volatile (chloro)hydrocarbons. Although HCOOH was also detected in low yields (2−8%) as a common photoproduct, it is doubtful that the amount of HCOOH directly reflects the photodecomposition (at the C−C bond α to carboxyl group) of the amino acids, because it is reported that the hydroxycarbonyl radical (•COOH) is unstable and readily decomposes to give carbon dioxide.[42] Therefore, Gly and hydrocarbons on one hand and hydroxycarboxylic acids and ammonia on the other hand are thought to be the major products that may provide insights into the photodecomposition mechanisms at pHs 1 and 7, respectively.

The formation of Gly and volatile products upon photodecomposition of Val, Leu, and Ile at pH 1 is reasonably accounted for in terms of the Norrish type II mechanism (Scheme 2),[24,43] which is well established for excited ketones possessing a hydrogen at the γ-position but has not been proposed for excited amino acids. Thus, for example, the excited carboxyl group of Leu abstracts the γ-hydrogen through a six-membered transition state, and the resulting 1,4-biradical undergoes β-cleavage at the C2−C3 bond, giving the Gly

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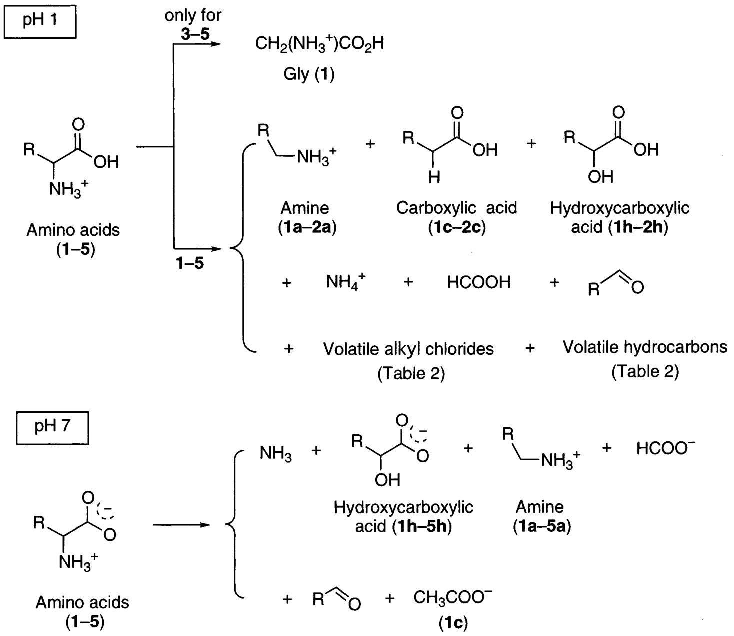
(42) Givens, R. S.; Levi, N. In *The photochemistry of organic acids, esters, anhydrides, lactones and imides*; Patai, S., Ed.; John Wiley & Sons: New York, 1979; p 641.

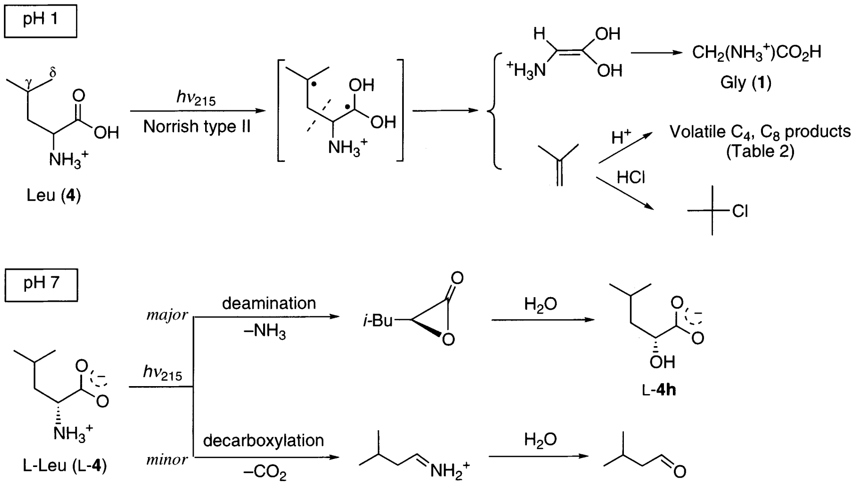
(43) Wolff, G.; Ourisson, G. *Tetrahedron Lett.* **1981**, *22*, 1441.

Scheme 1. Photodecomposition Products of Amino Acids[a]



[a] R = H (**1**), CH_3 (**2**), *i*-Pr (**3**), *i*-Bu (**4**), *sec*-Bu (**5**).

Scheme 2. Photodecomposition Mechanism of Leu Irradiated at 215 nm



tautomer and isobutene. The isobutene gives volatile products (Table 2) via acid-catalyzed processes at pH 1.

The isotropic and anisotropic transitions that determine the UV and CD spectra in Ala, and the isotropic transitions of the UV spectra in Gly, are similar to those of Leu.[36−38] The absorption at 215 nm is assigned to the n,π^* transition of the carboxyl group. The difference in the molecular structures of Gly, Ala, and Leu is that Gly and Ala do not have γ-hydrogens that can be abstracted by the excited carboxyl group. This is the reason why the conversions are significantly lower for Gly and Ala and the production of ammonia and hydroxycarboxylic acids becomes the major photoprocess; therefore, many researchers have thought photodeamination to be the main mechanism for various amino acids (Scheme 3, top path).[28,29,34] In addition, Gly and Ala undergo a minor photodecarboxylation path to the corresponding alkylamines **1a** and **2a** in low yields (5−15%) (Table 1), probably via a Norrish type I mechanism, at least at pH 1, which would also rationalize the formation of aldehyde (Scheme 3).

At pH 7, the n,π^* transition of the carboxyl group (carboxylate anion) contributes to the UV and CD absorption at 215 nm.[36−38] Ammonia and hydroxycarboxylic acids are the main products of the photodecomposition of amino acids in neutral solutions irradiated at 215 nm (Table 1). The yields of HCOOH and aliphatic amines (**3a**−**5a**) were small. Similar photodecomposition was reported to occur upon irradiation of acetic acid, which gives methane and carbon dioxide at pH 1, and methane, methanol, HCOOH, and carbon dioxide at pH 7, although the detailed mechanisms were not fully established.[42,44]

To further investigate the photodeamination mechanism of the amino acids, we examined the photodecomposition of isoamylamine **4a**. **4a** was photoirradiated at 215 nm at pHs 1 and 7, but did not produce any ammonia or isoamyl alcohol (initial concentration, 3.79 mM (pH 1.05) and 3.56 mM (pH 6.32); dose, 60.1 mA h (pHs 1.05 and 6.32); conversion, 12.1% (pH 1.05) and 16.1% (pH 6.32). This suggests that the carboxylic and carboxylate groups are first excited and that the

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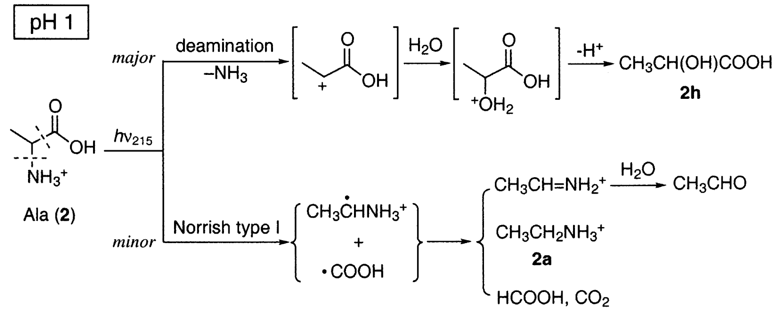
(44) Mittal, L. J.; Mittal, J. P.; Hayon, E. *J. Phys. Chem.* **1973**, *77*, 1482.

Scheme 3. Photodecomposition Mechanism of Ala Irradiated at 215 nm



excited carboxyl group plays a crucial role in the photodeamination, because in Leu the UV absorption from 200 to 250 nm arises from the *n*,π^* transition of the carboxyl (carboxylate). If the deamination occurs via electron transfer, α-radicals of isovaleric acid (**3c**), 4-methylvaleric acid (**4c**), and 3-methylvaleric acid (**5c**) would be generated,[45] and the corresponding carboxylic acids should be produced. In the solid state, it is detected by ESR that the α-radical of the amino acid is produced by photoirradiation.[46,47] However, the corresponding carboxylic acids (**3c**−**5c**) were not detected in our experiments. Thus, in solution, the radical mechanism is not thought to be the main photodecomposition pathway (Scheme 3), although the deamination is triggered by the photoexcitation of the carboxylic (carboxylate) moiety of the amino acid, irrespective of solution pH.

For the production of aldehyde, the secondary photoreaction of hydroxycarboxylic acid (**Xh**) is responsible, at least in part, since **4h** is reported to photodecompose to the corresponding aldehyde in low yield.[41,48] However, considering the produced amounts, hydroxycarboxylic acids are not thought to be the source of aldehyde. Probably decarboxylation of amino acid occurs to give the relevant imine, which then reacts with water to give the corresponding aldehyde (Scheme 3). Irrespective of solution pH, however, the *n*,π^* transition of the carboxylic (carboxylate) group determines the photodecomposition for this series of amino acids.

It is puzzling that acetic acid (**1c**) is consistently produced in varying yields, irrespective of amino acid or solution pH. At present, we have no rationale for such unselective, unstable production of **1c** upon irradiation of amino acids in aqueous solutions at various pHs. The formation mechanism does not appear to be simple or single, but rather it varies depending upon amino acid structure and solution pH. For example, we can postulate ketene as a precursor to **1c** upon irradiation of Val and Ile, since the 1,4-biradical derived from the Norrish type II reaction may cyclize to *gem*-cyclobutanediol, which is dehydrated under acidic conditions to give cyclobutanone, which is then photodecomposed to ketene.[49−51] In the case of Leu, a similar mechanism leads to the formation of dimethylketene and then isobutyric acid, which should be detected indeed in the reaction mixture at pH 1. However, the production of isobutyric acid was not detected by ion chromatography and capillary electrophoresis.

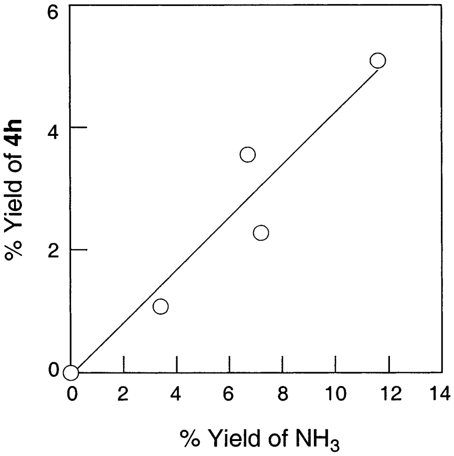


Figure 6. Relationship between the photoproduction of ammonia and hydroxycarboxylic acid **4h** in the case of Leu irradiated at pH 7; data taken from Table 1.

Excitation Wavelength-Dependent Photodeamination at pH 7. To examine the excitation wavelength effect on the mode and efficiency of photodecomposition, the photolyses of Leu at 200 nm, instead of 215 nm, were performed at pHs 1 and 7. The relative CPL or LPL intensity at 200 and 215 nm was close to unity ($I_{200}/I_{215} = 1.075$).[27,52] At pH 1, the absorbance of Leu does not greatly differ at these two wavelengths ($A_{200}/A_{215} = 1.14$), and the conversion and the Gly yield were practically the same at 200 and 215 nm (Table 1). Hence, no significant change appears to occur in the excited state and reaction mechanism involved.

At pH 7, the absorbance ratio becomes much greater ($A_{200}/A_{215} = 4.9$; $\epsilon_{200}/\epsilon_{215} = 158.2/33.6 = 4.7$), but the conversion was only slightly (7%) increased at 200 nm, indicating a lower quantum efficiency at the shorter wavelength. However, the production ratio of NH_3 and hydroxycarboxylic acid **4h** to the total decomposition was much enhanced (Table 1). Probably, the use of a shorter wavelength causes a more efficient (selective) excitation of the carboxylate chromophore, leading to the more selective deamination.

It is interesting to mention that, irrespective of irradiation wavelength, the production of NH_3 correlated with that of **4h** (Figure 6). This means that photodeamination takes part in the production of hydroxycarboxylic acids.[29,33]

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(45) Garrison, W. M. *Chem. Rev.* **1987**, *87*, 381.
(46) Johns, R. B.; Looney, F. D.; Whelan, D. J. *Biochim. Biophys. Acta* **1967**, *147*, 369.
(47) Neta, P.; Simic, M.; Hayon, E. *J. Phys. Chem.* **1970**, *74*, 1214.
(48) Mclaren, A. D. *Photochemistry of enzymes, proteins, and viruses*; Interscience Publishers: New York, 1949; Vol. IX.
(49) Turro, N. J. *Modern Molecular Photochemistry*; Benjiamin/Cummings Publishing: New York, 1978.
(50) Turro, N. J.; Farneth, W. E.; Devaquet, A. *J. Am. Chem. Soc.* **1976**, *98*, 7425.
(51) Dalton, J. C.; Dawes, K.; Turro, N. J.; Weiss, D. S.; Barltrop, J. A.; Coyle, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 7213.
(52) Farge, Y. *Appl. Opt.* **1980**, *19*, 4021.

pH Dependence of the op and Production of Gly. Figure 3b shows the decomposition of Leu and the production of Gly upon CPL irradiation of the same dose (60 mA h) at various pHs. The solid line depicts the pH dependence of the % yield of Gly based on the total decomposition of Leu, while the dotted line depicts the pH dependence of the % decomposition of Leu. It can be seen that the profiles of the lines that depict the pH dependence of the % op (Figure 3a), which was evaluated from the CD measurement, correspond with those in Figure 3b; probably the slow decomposition of Gly enables us to observe the relationship. Considering the pH dependence of the composition of ionic species of Leu (Figure 3c), it is the n,π^* transition of the carboxyl group of Leu that determines the pH dependence of the % op and the photodecomposition at pH 1. At pH 1, the AAP of Leu with CPL proceeds according to Kagan's equation, where the photodecomposition proceeds via a Norrish type II mechanism. The situation for Ala is very similar to that of Leu.

Photoracemization and Stereoselectivity of the Chiral Product. The origin of the zero op at pH > 6 (Figure 3) is left unanswered. It was reported that the photoracemization from L-Ala does not occur.[29] However, strictly speaking, this is not correct. HPLC analyses using a chiral column showed that photoracemization of L-Leu and L-Ala does indeed occur, albeit in trace amounts. At pH 7, the yields of D-Leu and D-Ala based on conversion (total decomposition) were 1.5% and 2.0%, respectively (Figure 5). Thus, the photoracemization does occur but can account for only 2% of the reacted amino acids. Therefore, the extent of the observed photoracemization is not enough to result in zero op of Leu and Ala irradiated at pH 7.

The product analysis confirmed that Ala, Val, and Leu photochemically produce their corresponding hydroxycarboxylic acids (**2h**−**4h**) as chiral products. In the case of Ala, Weizmann and co-workers reported that the photodeamination of L-Ala produced the α-carbocation of the corresponding carboxylic acid. The α-cation reacts with water to give the hydroxycarboxylic acid. They suggested that a so-called photoracemization occurred.[31,32] On the other hand, McLaren and co-workers reported that the photodeamination of L-Ala produced an α-lactone (D-form), and the α-lactone hydrolyzed to give L-**2h**;[29,33] thus, the photoproduction of **2h** was stereoselective. The sign of the CD of L-Ala ((*S*)-(+)-Ala) is the same as that of L-**2h** ((*S*)-(+)-**2h**).[37,39] The sign of the CD of L-Leu ((*S*)-(+)-Leu) is the same as that of L-**4h** ((*S*)-(−)-**4h**).[41] If L-**4h** is stereoselectively produced when the L-Leu ((*S*)-Leu) in Leu is preferentially excited by *l*-CPL, the enantiomeric enrichment of D-Leu ((*R*)-Leu) does occur, but its CD signal is diminished or even canceled by the opposite-signed CD signal of the produced L-**4h**.

Figure 5b shows that L-Leu, irradiated with LPL at 215 nm, photochemically produced D-**4h** ((*R*)-**4h**) and L-**4h** (D-**4h**/L-**4h** ≈ 1/3) at pH 7; in the case of D-Ala, D-**2h**/L-**2h** ≈ 8/5. It was difficult to estimate D-**4h** and L-**4h** because the production quantity was low. However, it is clear that L-**4h** was preferentially produced by the photodecomposition of L-Leu, which was thought to be applicable for the Ala case.[29] Considering the stereoselectivity of photoproduction of **4h** and the fact that the photoracemization of Leu scarcely proceeded, **4h** and NH_3 are produced by a typical concerted reaction through the α-lactone intermediate (Scheme 2), which is largely in agreement with McLaren's explanation.[29,33]

Considering the stereoselectivity of **4h**, an ee should be present; an op is apparent (Figure 3a), and at pH 1 the production of **4h** was low, so the op's are effectively equal to ee's. The form of the carboxylic acid moiety of the amino acid (pH-dependent) switches the photodecomposition mechanism and determines the op as estimated using CD and the conversion in the pH range from 1 to 7.

CPL Photolysis of Amino Acid as a Simultaneous Asymmetric Photodestruction/Production. The APP of *rac*-Leu and *rac*-Ala produces optically active products. Therefore, the AAP of amino acids may be differentiated from the conventional asymmetric photodestruction, in which the product is usually achiral.[9,21]

In our recent papers,[53−55] we proposed a new category of AAP, in which the irradiation with *l*- or *r*-CPL of a racemic reactant leads to the synchronous enantiomeric enrichment of both reactant and product. This AAP has two subcategories: (a) reversible AAP (CPL excites both the reactant and the product) and (b) irreversible AAP (only the reactant is excited by CPL). In this type of AAP, the product is also chiral. In the present case, **4h** is chiral and itself does not photochemically produce Leu. The treatment for (b) irreversible AAP is thought to be directly applicable to the present case if the production of **4h** is quantitative and stereoselective.

When Leu is irradiated with *l*-CPL until the conversion reaches 8%, the theoretical θ_{215} is estimated to be −0.03 mdeg, using $g_{215} = 0.015$. In the irreversible AAP, the ee of the product at the initial stage is $g_{215}/2$ of substrate Leu. Therefore, if the production of **4h** is quantitative and stereoselective, the θ_{215} arising from **4h** in the case of Leu irradiated with *l*-CPL can be estimated as ~0.02 mdeg {$=\Delta\epsilon_{215}$ of L-**4h** ($=0.42\ \text{M}^{-1}\ \text{cm}^{-1}$) × 3300 × 10 × [Leu] (0.005 M) × conversion (=0.08) × production ratio of **4h** (=0.13) × path length (=0.5 cm) × ee of **4h** (~0.0075)}.[41,53] We should consider that the θ arising from enriched D-Leu is affected by the θ arising from enriched L-**4h**. The approach to the situation of Leu irradiated with *r*-CPL is the same as that for Leu irradiated with *l*-CPL. The stereoselectivity in the production of **4h** is high, the CD of **4h** effectively diminishes the CD of the AAP of Leu, and the apparent CD_{215} becomes undetectable.[36,41] Therefore, we conclude that the CD of **4h** produced by the photodecomposition of Leu decreased the op of the Leu irradiated at pH 7. At pH 1, **4h** was scarcely produced by irradiation. This is the reason why AAP of Leu occurs via CPL irradiation at pH 1. Changing the solution pH from 1 to 7, the photodecomposition mechanism of Leu changes from Norrish type II to photodeamination, and the main product changes from Gly to **4h**. This is the reason why each observed op deviated from the theoretical value according to the solution pH.

Hydroxycarboxylic Acids Contained in Meteorites. The pH of the medium is critically important when we consider the environment in which AAP proceeds;[1,56] this is especially so when considering the generation of enantiomerically enriched

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samples of amino acids found in meteorites, and the implication on the biosphere's amino acid homochirality. In the recent report on sugar-related compounds found in carbonaceous meteorites, Cooper et al. have shown that the aqueous meteorite extracts are neutral to slightly alkaline, pH 7−9.[57] The basic condition is favorable for the formose reaction, which is thought to be responsible for the extraterrestrial synthesis of sugar-related compounds, although such a thermal process intrinsically requires reasonable temperature to proceed. Similarly, the Strecker synthesis preferentially produces amino acids at high ammonia concentrations.[20]

As demonstrated in the present study, the CPL photolysis of amino acids does lead to an enantiomeric enrichment in the remaining amino acid not only at acidic pH[24,25,36] but also at neutral to basic pHs, as far as the enantiomer-selective photoexcitation by CPL takes place. Consequently, Bonner's hypothesis, claiming the AAP of racemic amino acids as an origin of homochirality in the biosphere,[1] and the formose reaction as a source of the sugar-related compounds found in carbonaceous meteorites[57] do not conflict but rather are compatible with each other in view of the environmental pH required for the processes. However, the present study has revealed also that the hydroxycarboxylic acids produced by AAP of amino acids under neutral to basic conditions are optically active, which clearly conflicts with the fact that hydroxycarboxylic acids contained within the Murchison meteorite are racemic.[20] Our tentative conclusion is, therefore, that the AAP of amino acids occurred not on the Murchison meteorite at neutral to basic pHs but on its precursor under more acidic conditions, or rather that the AAP took place at neutral or basic pH to produce optically active hydroxycarboxylic acids, which then suffered from subsequent thermal racemization. The latter may be compatible with the report that alkyl phosphonic and sulfonic acids were extracted from the Murchison meteorite,[58,59] and further suggests that the pH of the precursor is not the same as that of the Murchison meteorite itself.

Conclusions

In conclusion, the enantiomeric enrichment of Leu and Ala by *l*- or *r*-CPL irradiation was pH-independent. At pH 1, the op's (=ee's) were obtained according to Kagan's equation. At pH 7, an op of Leu and Ala irradiated at 215 nm was not observed. However, these are only apparent op's, as the enantiomeric enrichment of Leu and Ala does proceed by CPL irradiation at all pHs, but the CDs from the AAP of Leu and Ala were diminished or canceled by the CD of the photoproducts **4h** and **2h**.

At pH 1, in the case of amino acids having a γ-hydrogen such as Leu, the photodecomposition proceeds mainly via a Norrish type II mechanism and gives Gly as the main product. In the case of amino acids having no γ-hydrogen, the photodecomposition proceeds much more slowly via the photodeamination mechanism and a Norrish type I mechanism. In both cases, the n,π^* transition of the carboxylic acid is responsible for the photodecomposition.

At pH 7, regardless of the type of amino acid, the photodecomposition mechanism is mainly photodeamination. It is confirmed that the photochemical racemizations of Leu and Ala scarcely proceed, and that 2-hydroxycarboxylic acid is stereoselectively produced. The n,π^* transition of the carboxylate anion is responsible for the photodeamination. The photodeamination and the production of **4h** are a stereoselective concerted reaction. These yields are also irradiation wavelength-dependent.

This work addresses speculations reported in our previous paper.[24] If CPL irradiation is a trigger for the homochilarity of biomolecules (amino acids), then the pH of the medium is not critically important. The Murchison and Murray meteorites contained many organic materials such as hydroxycarboxylic acids; by applying the approach discussed above, nonracemic hydroxycarboxylic acids should be produced by CPL irradiation. It is hoped that these results help to address problems arising from the potential origin of homochirality of biomolecules by this process.

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Supporting Information Available: Product analysis of **4h** irradiated by LPL; conversion dependence of % ee upon irradiation of Leu with CPL; UV and CD spectral changes of L-Leu and D-Ala under alkaline conditions; CD spectra of L-**4h**; and simulated CD of Leu irradiated by *l*-CPL using the CDs of D-Leu and L-**4h** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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