

PHOTOCATALYTIC SYNTHESIS OF L-PIPECOLINIC ACID FROM N ϵ -CARBAMYL-L-LYSINE BY AQUEOUS SUSPENSION OF PLATINIZED TITANIUM(IV) OXIDE

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Abstract—Photoirradiation at > 300 nm onto a suspension of platinized TiO_2 ($\text{TiO}_2\text{-Pt}$) particles in an aqueous solution of N ϵ -carbamyl-L-lysine ($\text{Lys}(\text{CONH}_2)_2$) induced the selective N-cyclization of $\text{Lys}(\text{CONH}_2)_2$ into almost optically pure L-pipecolic acid (PCA) under argon atmosphere at ambient temperature. Among various $\text{TiO}_2\text{-Pt}$ catalysts, a P-25 (Degussa) powder platinized via impregnation from chloroplatinic acid followed by hydrogen reduction at 753 K exhibited the highest photocatalytic activity for $\text{Lys}(\text{CONH}_2)_2$ consumption and L-PCA production. GC-MS analyses of L-PCA obtained photocatalytically from ^{15}N - α - $\text{Lys}(\text{CONH}_2)_2$ revealed the selective formation of ^{15}N -substituted L-PCA. This implies that the mechanism for L-PCA production contains selective cleavage of C ϵ -N bond and intramolecular alkylation at α -amino group. Effect of pH on the rate of this photocatalytic reaction was investigated in detail and compared with the pH-dependent charge distribution in $\text{Lys}(\text{CONH}_2)_2$ molecule. It is clarified that protonation-deprotonation of α -amino group gives marked influence on the rate and selectivity of the photocatalytic reaction. On the basis of these results, it is concluded that the selective production of optically pure L-PCA, especially in an acidic suspension of $\text{TiO}_2\text{-Pt}$, was attributed to the enhanced protonation of α -amino group to prevent undesirable oxidation by photogenerated positive holes and blocking of ϵ -amino group to yield racemic Schiff base intermediate.

INTRODUCTION

L-Pipecolic acid (L-piperidine-2-carboxylic acid, L-PCA)[†] is a basic skeleton of various types of naturally occurring piperidine alkaloids and relating drugs, and has been used as a precursor for their synthesis.¹ For example, N-propyl-L-pipecolic acid 2,6-xylidide has prepared from PCA as a local anesthetic.^{2,3} Since PCA is a non-proteinogenic imino acid, its abundance, generally in the form of L-(S)-isomer, in natural products seems too small to extract in practical industrial processes. Therefore, the plausible strategy for obtaining optically active PCA includes resolution of racemic PCA prepared

from pyridine-2-carboxylic acid or chemical synthesis from optically active compounds. Several examples, as latter cases, of PCA synthesis from L-lysine (Lys) have been reported.^{4–6} Although the use of such easily available source material is much advantageous, these synthetic routes required the use of stoichiometric amount of reagents and, moreover, most of them involve multiple steps, which reduce the overall yield of L-PCA.

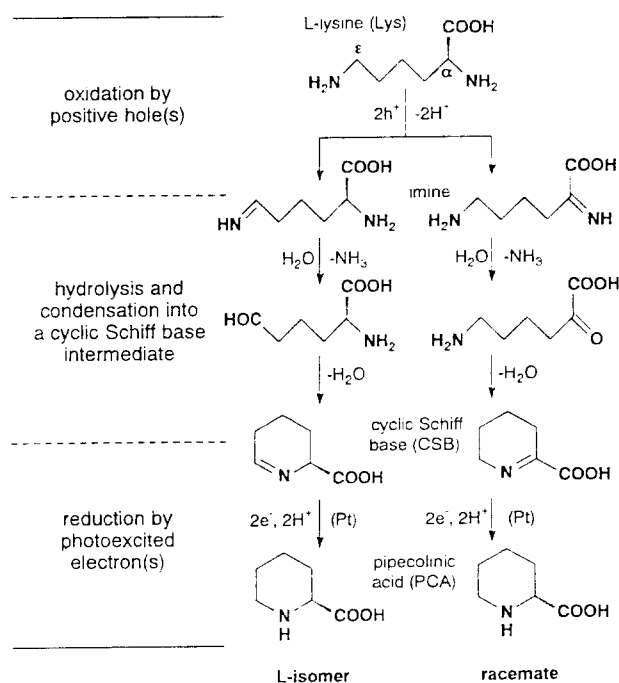
The recent report from our laboratory has shown that PCA is obtained from Lys through one-step photocatalytic reaction with aqueous suspension of semiconductor particles.⁷ The photocatalytic reaction can be operated at room temperature and ambient pressure, and requires no sacrificial reagent; the reaction proceeds catalytically in the presence of semiconductor particles under photoirradiation. As interpreted previously and shown also in Scheme 1, the overall process of photocatalytic production of PCA from Lys consists of three steps. First, positive holes (h^+) are produced by photoexcitation of valence-band electrons of semiconductor particle into its conduction band, and oxidize one of amino groups to yield imines. They are hydrolyzed in an aqueous solution into α -keto acid or δ -aldehyde,

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† Abbreviations: $\text{TiO}_2\text{-Pt}$, platinized titanium(IV) oxide powder; $\text{Lys}(\text{CONH}_2)_2$, N ϵ -carbamyl-L-lysine; PCA, pipecolic acid (piperidine-2-carboxylic acid); Lys, L-lysine; CSB, cyclic Schiff base; TEM, transmission electron micrograph; GC, gas chromatography; HPLC, high-performance liquid chromatography; PDN, piperidine; NMR, nuclear magnetic resonance spectroscopy; MS, mass spectroscopy; EI, electron impact; CI, chemical ionization; TMS, trimethylsilyl.

and their residual amino groups undergo intramolecular condensation with the carbonyl group in the opposite side into cyclic Schiff base (CSB) intermediates. The photoexcited electrons (e^-) reduce CSB's, along with addition of protons (H^+), to the final product, PCA. Thus, equal numbers of h^+ and e^- are used for the PCA production. This reaction, therefore, proceeds catalytically, *i.e.*, without change in the semiconductor particles. Furthermore, neither sacrificial reagents are needed nor by-products are formed in principle. Among various semiconducting materials, titanium(IV) oxide (TiO_2) and cadmium sulfide (CdS) are often used as a photocatalyst and showed sufficient activity toward the PCA production. However, they give different products; TiO_2 and CdS produced L-excess and racemic PCA, respectively. This catalyst dependence is due to the preferential oxidation of ϵ and α -amino groups by h^+ , respectively, though the origin of such selection in the oxidation step is ambiguous at present.

These results lead to a strategy, for selective production of optically active PCA, to enhance the reactivity of ϵ -amino moiety toward positive holes by its chemical modification. Preliminary experiments along this line have been succeeded in preparation of almost optically pure L-PCA from N_ϵ -substituted Lys, such as N_ϵ -carbamyl-L-lysine (L-homocitrulline, $Lys(CONH_2)$) or L-2-amino-6-guanidinohexanoic acid (L-homoarginine).⁷ This paper reports the further investigation on the photocatalytic synthesis of PCA from $Lys(CONH_2)$ trying to optimize reaction conditions and photocatalysts, and to clarify the mechanism.



MATERIALS AND METHODS

Materials. Commercial reagent-grade TiO_2 and CdS powders were used without further purification or activation unless otherwise stated. TiO_2 samples, Ti-HR-9 and Ti-HR-12, were offered from Degussa (Germany). Their crystal structure was analyzed by powder X-ray diffraction as described elsewhere.⁸ Loading of platinum onto the catalyst was made as follows. Impregnation:^{9,10} To an aqueous suspension (500 mL) of catalyst (4.9 g) was added dropwise an aqueous solution of chloroplatinic acid (H_2PtCl_6 , 490 mg). The suspension was evaporated and dried at 383 K for 2 h. The powder was heat-treated at 753 K under continuous hydrogen (H_2) stream (50 mL min^{-1}). Deposition from sol:^{11,12} A black-colored Pt sol was prepared by refluxing an aqueous solution (150 mL) of H_2PtCl_6 (30 mg) and sodium citrate (0.2%) for 4 h. After cooling, the sol was treated with an Amberlite MB-3 ion exchange resin in its H^+ and OH^- form for 1 h to remove excess citrate and inorganic electrolytes and filtered. Catalyst (0.47 g) was suspended in the resultant Pt colloid (50 mL), and 2.8 g of sodium chloride (NaCl) was added to precipitate the Pt particles. The suspension was stirred for 1 h at room temperature, washed with ion-exchanged water repeatedly, and dried *in vacuo*. Mechanical mixing: Given amounts of catalyst and Pt black (Wako) were mixed and brayed in an agate mortar for 15 min. Transmission electron micrographs (TEM) were recorded on a Hitachi H-800, operated at 175 kV of electron acceleration voltage. The details of sample preparation and measurement will be published elsewhere.¹³

$Lys(CONH_2)$ was prepared as hydrochloride from copper(II) salt of Lys with potassium cyanate,¹⁴ and recrystallized twice from water-ethanol in 42% yield as white crystals (mp 174–179°C, uncorrected; ref.¹⁴ 177–178°C). Anal. Calcd for $C_7H_{15}N_3O_3 \cdot HCl$: C, 37.26; H, 7.15; N, 18.62; O, 21.27; Cl, 15.71. Found: C, 37.19; H, 6.98; N, 18.58; O, 21.46; Cl, 15.80. ^{15}N - α -Lys($CONH_2$) was prepared similarly from ^{15}N - α -Lys (Cambridge Isotope Laboratories, 99% ^{15}N) in 60% yield as white crystals (mp 173–180°C). Optical purity (> 99%) of these products was confirmed by HPLC under the conditions as described below. Lys and authentic samples were supplied from Wako Pure Chemicals in best available grades. Ion-exchanged water prepared with a Corning MegaPure System MP-190 (> 16 M Ω cm) was used to make aqueous solutions unless otherwise described.

Photoirradiation and product analyses. A suspension of catalyst (50 mg) in an aqueous solution of Lys (100 μ mol, 5.0 mL) was placed in a test tube (18 mm \times 180 mm, transparent at > 300 nm) and purged of air by argon (Ar) bubbling for at least 20 min. The tube was sealed off with a rubber stopper and irradiated at 298 K (± 0.5 deg) under vigorous magnetic stirring (1000 rpm) with a 400 W mercury arc (Eiko-sha). After the irradiation, a portion (200 μ L) of gas phase of the sample was withdrawn with a syringe and subjected to gas chromatography (GC). The GC analysis conditions were as follows; a Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector and a 60–80 mesh molecular sieve 5A column (3 mm \times 3 m) with Ar carrier at 373 K for molecular hydrogen (H_2) measurements. A 50–80 mesh Porapak Q (3 mm \times 3 m) column was used with helium (He) carrier at 353 K for carbon dioxide (CO_2) analyses. The suspension was centrifuged to remove the catalyst and

analyzed by high performance liquid chromatography (HPLC). To measure the yields of enantiomers of PCA, piperidine (PDN), and ammonia (NH_3), a portion of sample solutions was treated with 2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylisothiocyanate (Wako) 20 min before injection to HPLC (Shimadzu LC6A) equipped with an ultraviolet absorption detector (250 nm). A mixture of 10 mM phosphate buffer and methanol (45:55 (v/v)) was made to flow through a reversed phase column (Cosmosil SC18-AR; 4.6 mm \times 250 mm, Nacalai Tesque) at 0.8 mL min^{-1} at 313 K. The molar amount of Lys(CONH₂) was measured by HPLC with a Daicel Chiralpak MA(+) column (4.6 mm \times 50 mm, at 318 K with 0.5 mM aqueous copper(II) sulfate solution).

Isolation of PCA was performed with five to twelve 5 mL samples obtained under the same photoirradiation conditions to consume Lys(CONH₂) almost completely. The samples were gathered and evaporated to dryness. ¹H-nuclear magnetic resonance spectroscopy (NMR, JEOL GSX-270, 270MHz, D₂O): δ = 1.3-2.0 (m, 5H), 2.3 (dd, 1H), 3.0 (td, 1H), 3.4 (d, 1H), 3.9 (dd, 1H). A contaminated HDO signal was used as an internal standard of chemical shift (4.76 ppm downfield from sodium trimethylsilylpropionate-d₄). L-PCA was also obtained and isolated from the reaction mixture of ¹⁵N-Lys(CONH₂) in HPLC yield 58% and 98% ee-L, isolated yield after recrystallization twice from water-ethanol, 11% and 99% ee-L (mp 247°C). GC-mass spectrography (MS) measurements were performed with a Shimadzu QP-1000EX equipped with a fused silica capillary (Shimadzu CBP-M25-025) eluted with He. Dried samples were treated with N-methyl-N-trimethylsilyltrifluoroacetamide (Pierce) in a sealed glass tube under nitrogen (N₂), heated at 403 K for 30 min, and injected. MS patterns of fraction were recorded in both electron impact (EI, 70 eV) and chemical ionization (CI, with isobutane) modes.

RESULTS AND DISCUSSION

Photocatalytic activities of semiconductor particles

Table 1 shows representative results photocatalytic reaction. TiO₂ powders, irrespective of their supplier and grade, gave PCA when loaded with appropriate amount of Pt, as reported previously.⁷ Compared with the rather poorer optical purity (around 60%) of PCA obtained from Lys, almost optically pure PCA could be synthesized from Lys(CONH₂). Ammonia (NH₃), hydrogen (H₂) and piperidine (PDN) were obtained as by-products. Bare TiO₂ powders showed negligible photocatalytic activity; neither consumption of Lys(CONH₂) nor production of PCA was observed. Such phenomenon is often seen for the photocatalytic reaction under deaerated conditions, and could be attributed to relatively higher activation energy for reduction of Schiff-base intermediate (as described later) or for H₂ evolution by photoexcited electrons at the bare TiO₂ surface. This leads to deactivation (recombination) of photoexcited electron-hole pairs and to negligible photocatalytic activity in the absence of adequate electron acceptor, e.g., molecular oxygen (O₂). Loading of Pt should induce lowering of the activation energy and facilitate the overall photocatalytic reactions.

Among TiO₂-Pt photocatalysts used in this investigation, TiO₂ powders containing anatase crystallites, especially P-25 TiO₂ particles, showed rather higher photocatalytic activity to convert Lys(CONH₂). TiO₂'s consisting of rutile crystallites only were

Table 1. Photocatalytic activities of TiO₂-Pt for L-PCA production from aqueous solution of Lys(CONH₂) under Ar*

run	substrate	TiO ₂ †		Pt loading ‡			conversion and product yield(%)§						
		code	cryst.	wt%	method	temp.(K)	conv.	PCA	(%ee-L)	H ₂	CO ₂	PDN	NH ₃
1	Lys	P-25	A+R	2	i	753	96	68	58	36	2	17	54
2	Lys(CONH ₂)	P-25	A+R	2	i	753	98	75	94	50	16	4	18
3	Lys(CONH ₂)	P-25	A+R	2	i	473	95	67	93	77	25	7	22
4	Lys(CONH ₂)	Merck	A	2	i	753	44	21	99	48	13	1	18
5	Lys(CONH ₂)	Merck	A	0.8	c	—	77	58	97	42	15	4	—
6	Lys(CONH ₂)	Ti-HR-9	A+R	2	m	—	46	30	99	23	15	9	—
7	Lys(CONH ₂)	Ti-HR-12	A	2	i	753	52	17	99	50	29	11	—
8	Lys(CONH ₂)	Furuuchi	A+R	2	i	753	81	43	99	77	24	8	—

* TiO₂-Pt catalyst (50 mg) was suspended in an aqueous solution of Lys (run 1) or Lys (CONH₂) HCl (runs 2-8) (0.10 mmol, 5.0 mL) and photoirradiated at > 300 nm for 3 h (run 1) or 6 h (runs 2-8) under vigorous magnetic stirring under an Ar atmosphere.

† Code (or name of the supplier) and crystallite structure (A: anatase and R: rutile).

‡ Amount and method for Pt loading; i: impregnation followed by H₂ reduction, the temperature of which is shown, c: mixing and precipitation from Pt sol, and m: mechanical mixing with Pt black (Wako) in an agate mortar. Symbol — denotes no heat treatment.

§ Based on feed(100 μ mol). Symbol — denotes failure in measurements due to interference by unknown product(s) in the HPLC analyses.

practically inactive for both Lys(CONH₂) conversion and L-PCA production even if they were loaded with Pt. A little lower conduction band energy, *i.e.*, poor reducing ability of photoexcited electron in the rutile crystal compared with that of anatase may account for such difference.¹⁵ Thus, the crystal structure of TiO₂ is one of the decisive factors for its photocatalytic activity, as often observed and discussed.⁸ Inspection of the results in Table 1 leads to the fact that amount and method of Pt loading also affect the Lys(CONH₂) conversion and L-PCA yield; in the case of Merck TiO₂, Pt loading from Pt colloid was preferable to impregnation, and temperature for H₂ treatment following to impregnation also gave a little influence on the photocatalytic activity of P-25 TiO₂. Practically, P-25 TiO₂ loaded with 2wt% Pt by impregnation followed by H₂ treatment at 753 K was the best suitable photocatalyst and used in the following experiments.

Fig. 1 is a TEM photograph of the platinized P-25 TiO₂ catalyst. It is seen that fine Pt particles (observed as black dots) the size of which ranged over 1-2 nm were deposited on 20-40 nm particles of TiO₂. The relatively larger surface area of P-25 TiO₂ particles, leading to larger amount of adsorbed reaction substrates, and well-dispersed Pt, causing effective reduction of intermediate species, may be the reason for the high photocatalytic activity toward the L-PCA synthesis. The details, *e.g.*, kinetic investigation in relation with physical properties of the photocatalyst, are reported elsewhere.¹³

The photocatalytic synthesis of L-PCA by commercial CdS powders, loaded with or without Pt (or its oxide, PtO₂ (Wako)) failed; Lys(CONH₂) was consumed with the rate a little smaller than that by

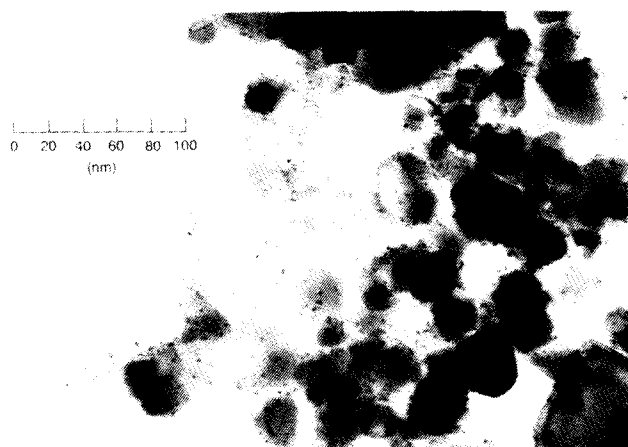


Figure. 1 The TEM picture of TiO₂(P-25) loaded with 2wt% Pt by impregnation from H₂PtCl₆ followed by heat treatment at 753 K under continuous H₂ stream.

TiO₂-Pt but negligible PCA yielded (data not shown). The product(s) has not been identified. Since the selective oxidation of α -amino group in Lys has been observed for CdS-based photocatalysts, one of the most probable products from Lys(CONH₂) is its α -keto acid, formed through oxidation of α -amino group followed by hydrolysis of resulting imino acid (see the following section).

Stoichiometry and mechanism of photocatalytic reaction of Lys(CONH₂)

Fig. 2 shows parts of GC-MS patterns (EI mode) of PCA synthesized photocatalytically from ¹⁵N-Lys(CONH₂) and its authentic sample. A peak at *m/z* 156 of the latter is assigned to a fragment of bis(trimethylsilyl) (TMS) derivative of PCA, (M - COOTMS)⁺, and peaks at 157 and 158 to its higher isotopic isomers. It is clear by comparison of MS pattern of the synthesized PCA with this standard that the product gave a fragment of one atomic unit larger molecular weight, as well as a small amount of the same basic fragment. This should be caused by the incorporation of ¹⁵N atom in PCA molecules. On the assumption that isotopic fraction (*m/z* 156 : 157 : 158 = 100 : 18 : 6) in the authentic sample is also applicable to the ¹⁵N-incorporated fragment, content of ¹⁵N-PCA in the photocatalytic product was evaluated to be 97%. Almost same result (96% ¹⁵N) was obtained for parent peaks of the same GC fraction (*m/z* 274 and 275 for the authentic and the products, respectively; (M + 1)⁺) appeared by CI method.

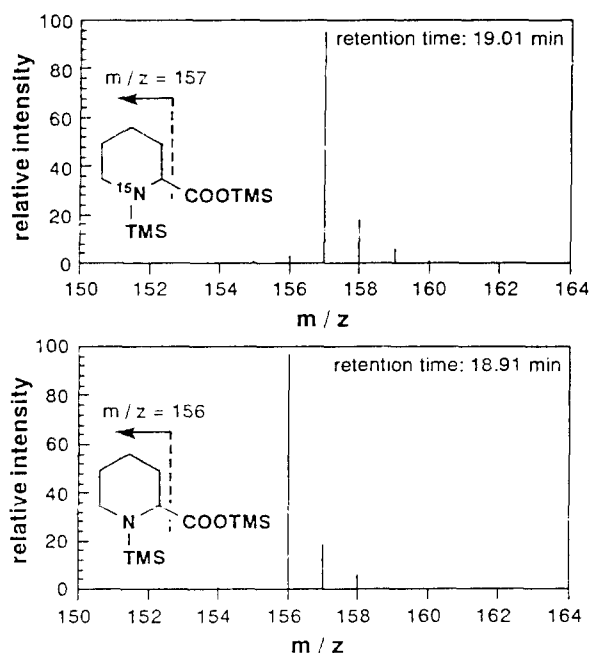


Figure. 2 GC-MS patterns of TMS derivatives of PCA; photocatalytic product (upper) and authentic sample (lower).

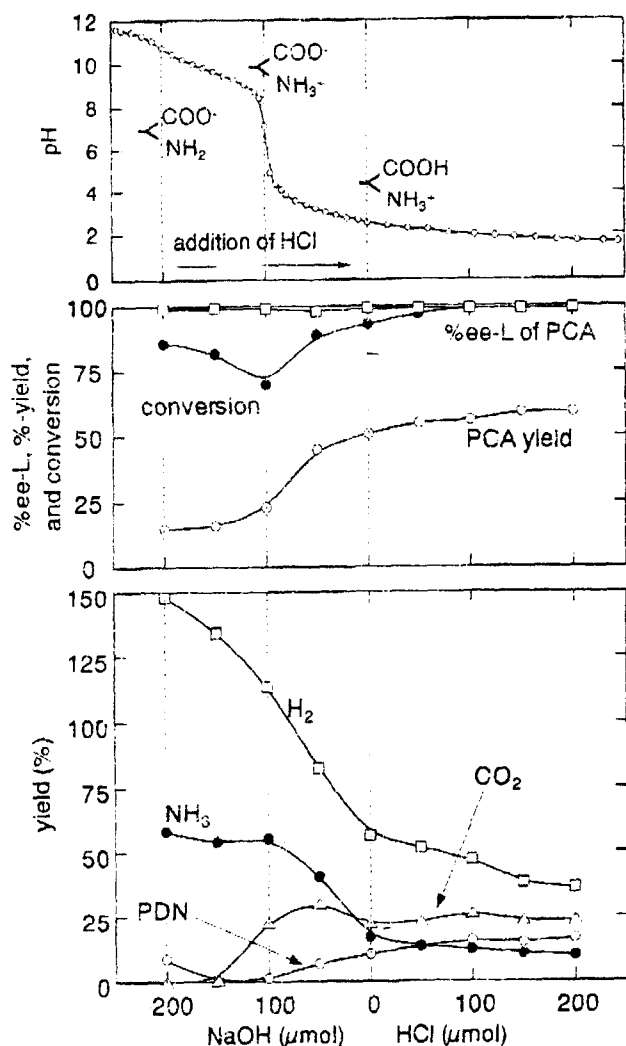


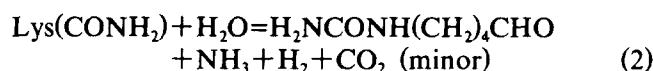
Figure. 3 Titration curve of aqueous $\text{Lys}(\text{CONH}_2)$ solution by HCl (upper) and effect of addition of NaOH and HCl on photocatalytic reaction (irradiation for 3 h) of $\text{Lys}(\text{CONH}_2)$ by $\text{TiO}_2\text{-Pt}$ suspension (middle and lower).

Thus, molar content of excess L-isomer (99% ee-L) was almost identical to that ^{15}N -isomer of PCA obtained photocatalytically. This clearly shows the selective inclusion of α -amino group of $\text{Lys}(\text{CONH}_2)$, *i.e.*, cleavage of $\text{C}_\epsilon\text{-N}$ bond during photocatalytic reaction. Neither the mechanism of this cleavage nor the fate of ureido group, is unambiguous at present. The stoichiometry is described formally as,

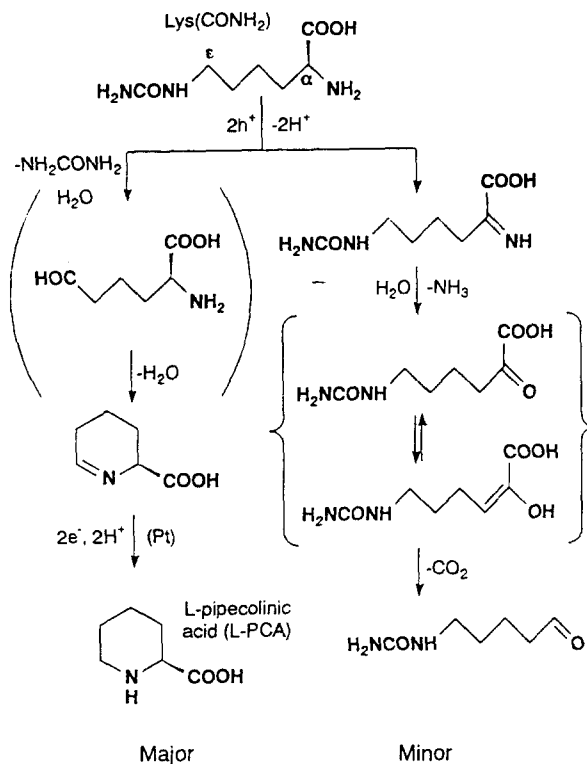


though we could not succeed in detecting urea in the photoirradiated reaction mixture by HPLC due to the interference by PCA. Anyway, we can presume the mechanism of selective formation of L-PCA through oxidation of ϵ -ureido moiety of $\text{Lys}(\text{CONH}_2)$,

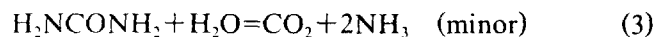
as shown in Scheme 2, on the analogy of photocatalytic reaction of Lys (Scheme 1). Thus, the carbamylation of ϵ -amino group of Lys may reduce the probability of oxidation at α -amino group. In the case that α -amino in $\text{Lys}(\text{CONH}_2)$ is oxidized first, intramolecular cyclization to a Schiff base intermediate can not be expected. Therefore, the resulting keto acid, in equilibrium with enol-acid, may undergo decarboxylation to yield aldehyde. In the reaction of Lys, similar aldehyde undergoes N-cyclization and reduction by the photoexcited electrons into PDN. That $\text{Lys}(\text{CONH}_2)$ produced less PDN and more CO_2 and H_2 (run 2) compared with Lys (run 1) is consistent with this speculation.



The formation of PND through decarboxylation of product PCA is rather unlikely since comparable or even larger amount of PCA was produced in the $\text{Lys}(\text{CONH}_2)$ system but PDN production was less marked. Furthermore, hydrolysis of product urea (reaction 3) in the reaction mixture during photocatalytic reaction should be a minor process, because only comparable or small amount of NH_3 could be detected (the CO_2 yield might be minimum due to its solubility in aqueous solutions).



Scheme 2



However, decomposition of urea, as well as the aldehyde, through oxidation by positive holes may account for the formation of excess amount of H_2 , though the detailed mechanism and stoichiometry are ambiguous.

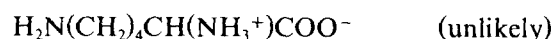
pH effect

Variation in $\text{Lys}(\text{CONH}_2)$ conversion, PCA yield, and optical purity of PCA, was shown in Fig. 3 (middle) as a function of molar amount of added sodium hydroxide (NaOH , 1 *M*) and hydrochloric acid (HCl , 1 *M*). Since hydrochloride of $\text{Lys}(\text{CONH}_2)$ was used as the starting material, center of the horizontal axis corresponds its acidic aqueous solution without any additives. Addition of NaOH up to 100 μmol , *i.e.*, equivalent to $\text{Lys}(\text{CONH}_2)$, reduced the conversion and the PCA yield, but influenced negligibly on the PCA optical purity. Further addition induced drastic decrease in the PCA yield, while the conversion recovered a little. On the other hand, addition of HCl gave negligible influence.

An aqueous $\text{Lys}(\text{CONH}_2) \cdot \text{HCl}$ suspension (50 mL with 3.0 mL of NaOH (1.0 *mM*); the concentrations of $\text{Lys}(\text{CONH}_2)$ and $\text{TiO}_2(\text{P-25})\text{-Pt}$ were same as in the photocatalytic reaction) was titrated with 1.0 *M* HCl (Fig. 3 upper, this was adjusted along the horizontal axis and compatible with the other plots). This shows that HCl salt of α -amino group is neutralized by the addition of NaOH (100 μmol) to form a zwitterion, and further addition leads to deprotonation of α -ammonium group, as depicted in the figure. The addition of HCl seems to give no structural change of $\text{Lys}(\text{CONH}_2)$. Because the basicity of ϵ -amino group of Lys is reduced markedly by carbamylation, a protonation-deprotonation equilibrium of ϵ -ureido group is not observed in this titration. Comparison of the structure with the pH dependence suggests that deprotonation of α -ammonium group decreases the PCA yield drastically (the lowered PCA yield at 100 μmol addition of NaOH may be interconnected with the decrease in $\text{Lys}(\text{CONH}_2)$ conversion). Lowered oxidation potential of α -ammonium group by its deprotonation may cause its preferential oxidation, rather than ϵ -ureido group to lead to L-PCA formation (reaction 1), by positive holes in TiO_2 . Therefore, in the basic suspension, reaction 2 might predominate in the photocatalytic process. The lower plots in Fig. 3 confirm this. The H_2 and CO_2 formations were enhanced markedly by the addition of alkali (the negligible apparent yield of CO_2 in gas phase, much smaller than expected from reaction 2, is caused by

absorption in the alkaline solutions).

It is elucidated that molar amount of PCA produced from Lys (Table 1, run 1) through oxidations of ϵ and α -amino groups were 39 and 29 μmol , assuming the formation of L- and racemic PCA, respectively. Because of the higher basicity of ϵ -amino group ($\text{p}K_a(\text{NH}_3^+)$: 10.28) compared with α -amino group (8.90), Lys in aqueous solution can not be in the form of



which is the most suitable structure for the selective oxidation at ϵ -amino group to yield optically pure PCA. Judging from the much increased yield of PCA *via* oxidation of the ϵ -ureido group (*e.g.*, minimum 70 μmol for run 2 in Table 1, while oxidation of α -amino group was evaluated to be maximum 23 μmol), the ϵ -carbamylation Lys prevents not only cyclization of α -keto acid to lead to racemic PCA but also oxidation of α -amino group by lowering relative basicity of ϵ -amino group to result in the formation of α -ammonium group.

The reason for the minimum $\text{Lys}(\text{CONH}_2)$ conversion and the PCA optical purity by the addition of equimolar amount of NaOH , *i.e.*, just neutralized conditions, is ambiguous. Almost zero net charge of $\text{Lys}(\text{CONH}_2)$ molecule at such pH conditions may affect the surface adsorption and reactivity.

CONCLUSION

It has been shown that almost optically pure PCA can be synthesized efficiently from $\text{N}\epsilon$ -substituted Lys by the photocatalytic reaction of platinized semiconductor particles. This is the first example, to the best of our knowledge, of application of semiconductor photocatalysis to the synthesis of optically active compounds. Further investigation on the photocatalytic organic syntheses *via* such redox-combined processes is now in progress.

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