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# Photoinduced Chemical Reactions on Natural Single Crystals and Synthesized Crystallites of Mercury(II) Sulfide in Aqueous Solution Containing Naturally Occurring Amino Acids

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Photoirradiation at >300 nm of aqueous suspensions of several natural crystal specimens and synthesized crystallites of mercury(II) sulfide (HgS) induced deaminocyclization of optically active or racemic lysine into pipecolinic acid (PCA) under deaerated conditions. This is the first example, to the best of our knowledge, of photoinduced chemical reactions of natural biological compounds over natural minerals. It was found that the natural HgS crystals had activity higher than those of synthesized ones but lower than those of other sulfides of transition metals, e.g., CdS and ZnS, belonging to the same II–IV chalcogenides. In almost all of the photoreactions, decompostion of HgS occurred to liberate hydrogen sulfide ($H_2S$) and $Hg^{2+}$, and the latter seemed to have undergone in-situ reductive deposition on HgS as $Hg^0$ after a certain induction period (24–70 h) during the photoirradiation, as indicated by the darkened color of the suspensions. The formation of PCA, presumably through combination of oxidation of lysine and reduction of an intermediate, cyclic Schiff base, could also be seen after a certain induction time of the $Hg^0$ formation. This was supported by the fact that the addition of small amount of $Hg^{2+}$ (0.5 wt % of HgS) increased the PCA yield by almost 2-fold. We also tried to elucidate certain aspects of the plausible stereochemical reactions in relation to the chiral crystal structure of HgS. Although, in some experiments, slight enantiomeric excess of the product PCA was observed, the excess was below or equal to the experimental error and no other supporting analytical data could not be obtained; we cannot conclude the enantiomeric photoproduction of PCA by the natural chiral HgS specimen.

## Introduction

Sulfides of metals have been extensively studied[1,2] as promising and easily available photocatalysts for a wide range of chemical reactions, including synthesis and conversion of useful organic chemicals.[3] Among the metal sulfides, mercury(II) sulfide (HgS) has rarely been reported to be photocatalytically active, while excellent activities of cadmium and zinc sulfide (CdS and ZnS), belonging to the same II−IV chalcogenides, have often been reported.[4] These II−VI binary compounds have either zinc blende or wurtzite structures. A noticeable exception is the case of HgS, which can be found either in the blende phase ($\beta$-HgS) or in a trigonal (space group $P3_121$ or $P3_221$) structure ($\alpha$-HgS, *cinnabar*). Although extensive investigations of the unique structure of HgS, including a study of long-wavelength vibrations,[5] measurement of the fundamental edge-absorption spectrum near the band gap,[6] calculation of the electronic energy levels,[7] and resonant Raman scattering measurements,[8] have been carried out, there have been no attempts of inducing chemical reactions influenced by its crystal structure. Due to the spiral arrangement[9] of atoms in the trigonal crystal structure,[10,11] the natural HgS crystal, cin-

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nabar, is chiral, similar to quartz, a famous natural chiral crystal. The surfaces of naturally occurring single crystals of HgS are expected to have unique surface chemistry that can be used for stereochemical reactions.

On the basis of these considerations, if HgS has photocatalytic activity, we can expect stereoselectivity in the reaction of organic compounds due to its optical activity. Stephens and co-workers first reported[12] the photocatalytic generation of hydrogen peroxide from an aqueous suspension of commercial and homemade HgS, and to the best of our knowledge, no reports on HgS photocatalysis have since been published. The band gap of HgS has been reported[6,13,14] to be ca. 2 eV, which is smaller than that of other metal sulfides and enables us to use light of a longer wavelength. On the basis of this aspect, the present work was undertaken in an attempt to show, for the first time, results of photoinduced amino acid synthesis (PCA from lysine) and the possible stereoselectivity of the products, if any, by photochemical reactions of naturally occurring single crystals and synthesized crystallites of HgS.

## Experimental Section

**Materials.** In this study, we used natural red-colored single crystals or their twin (named cinnabar A, B, C, ... to I) of cinnabar (specimens from Switzerland and China, supplied from Castle Jewelers and Nihonchikagakusha, Japan) and synthesized HgS (red and black) powders obtained from several commercial sources (including Wako, Kanto, Strem, Mitsuwa, and High Purity Chemicals, etc.). The natural crystals were used as received or, in most cases, crushed into powder in an agate mortar for photoinduced reactions. Amount of impurities in several HgS specimens were estimated roughly by ICP emission spectrometry (Perkin-Elmer OPTIMA 3300-DV) and ion chromatography (Shimadzu LC-10AD high-performance liquid chromatograph) after decomposition with aqua regia. BET surface area of a part specimens were measured at 77 K using a Quantachrome AUTOSORB-1 automated gas sorption system after drying at 473 K for 3 h. Optically pure and racemic lysine, PCA (99.9% purity), triethanolamine (TEOA), and mercury(II) chloride ($HgCl_2$, Wako) were used as received.

**Photoirradiation and Product Analysis.** Experimental runs were carried out using an argon- (Ar-) saturated aqueous suspension of HgS (50 mg except for the case of a lump) and a 5.0 $cm^3$ portion of aqueous solution of (*R*)- and (*S*)-lysine (racemic, 100 $\mu$mol, monohydrochloride salt neutralized by an equimolar amount of sodium hydroxide) in a test tube. It was then irradiated at 298 K under vigorous magnetic stirring (1000 rpm) with a 400-W mercury arc (Eiko-sha). After the reaction, the suspension was centrifuged to remove the particles and analyzed by high-performance liquid chromatography (HPLC) using a Daicel Crownpak CR(+) column (eluant, aqueous $HClO_4$ of pH 1.5; flow rate, 0.4 $cm^3\ min^{-1}$ at ambient temperature) and a Daicel Chiralpak MA(+) column (eluant, 0.1−2 mmol $dm^{-3}$ $CuSO_4$; flow rate, 0.4 $cm^3\ min^{-1}$ at ambient temperature) for lysine and PCA, respectively. A photocatalytic molecular-hydrogen ($H_2$) evolution reaction was carried out using a 5 vol % aqueous solution of TEOA (5 $cm^3$) and 50 mg of bare and platinum-loaded HgS (Wako) powders under Ar-purged deaerated conditions. The platinum loading onto HgS powders was made by deposition from Pt sol through salting-out or by photodeposition from an aqueous solution of hexachloroplatinic acid ($H_2PtCl_6$). Loading of Hg (0−2 wt %) was carried out by adding the required volume of an aqueous $HgCl_2$ solution to the reaction mixture of lysine and HgS powders. In some cases, a product PCA and unreacted lysine were separated and purified by ion exchange chromatography (weakly acidic IRC-50 and strongly acidic IR-120B resins) and thin-layer chromatography (TLC). Optical rotation (OR) and circular dichroism (CD) were measured after filtration of the centrifuged reaction solution with a 0.1 $\mu$m cellulose filter. In a photoirradiation experiment, a sample of natural crystal (cinnabar I) was treated with aqua regia before use to remove the contaminated impurity from the natural sources.

**Estimation of Quantum Efficiency.** Quantum efficiency of photoinduced reactions by HgS and CdS was estimated, in convenience, using the flux of incident photons of wavelength between 300 and 590 and 300−515 nm, respectively, by assuming that they absorb all the photons of energy greater than their band gap (2.1 and 2.4 eV, respectively). The incident photon flux was evaluated by total emission energy of the mercury arc at the sample position and a spectrum measured using a Molectron POWER MAX5200 laser power meter and a Hamamatsu Photonics C7473-36 photonic multichannel analyzer (resolution: 0.8 nm), respectively. Accurate determination of quantum efficiency using monochromatic light was failed due to negligible rate of photoinduced reaction under such weak light irradiation.

## Results and Discussion

**Crystal and Electronic Structures of HgS Specimens.** HgS exists in one of two structural forms: a trigonal (*cinnabar*) structure ($\alpha$-HgS, red) at room temperature, which transforms into cubic structure ($\beta$-HgS, black) at 617 K under atmospheric pressure. The cinnabar structure at room temperature makes HgS unique among II−IV chalcogenides. $\alpha$-HgS is characterized[8,10,11] by spiral chains, parallel to the *c*-axis. Six atoms arranged in a helical chain make up the unit cell in HgS, with Hg and S atoms alternately spaced along the chains. The chains join together to form a three-dimensional crystal as shown in Figure 1.

In this work, we have investigated the possible photoinduced organic reactions to determine the correlation of the stereoselectivity of the reaction products with the chirality of HgS. Before the investigation, we first tried to determine the ability of HgS to induce $H_2$ evolution under photoirradiation. The ability of a semiconductor to induce electron transfer to adsorbed species on its surface is governed by its band energy positions and redox potentials of reaction substrates. The relevant potential level of electron-accepting species is thermodynamically required to be below the conduction band potential of the semiconductor. The potential level of the electron donors (hole scavengers) must be above the valence band position of the semiconductor. The reported electronic structures of CdS and ZnS photocatalysts are shown in Figure 2, indicating appreciable photocatalytic activity for various reactions,[15] including $H_2$ evolution

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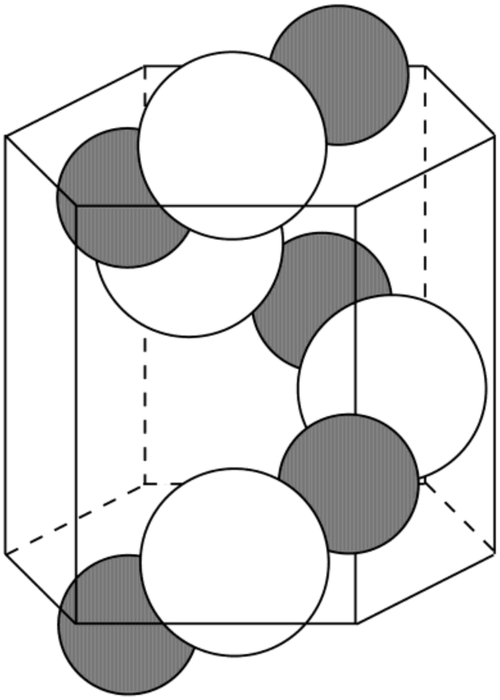

**Figure 1.** Crystal structure of mercury(II) sulfide in trigonal α-form.

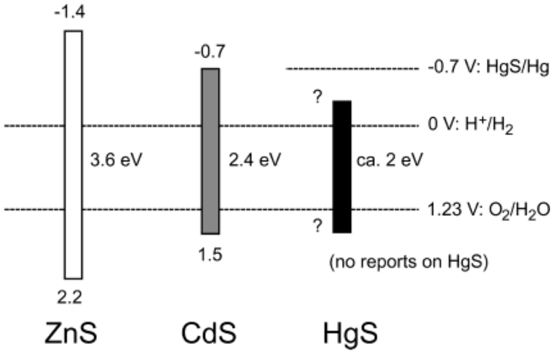

**Figure 2.** Reported band edge position of metal sulfides (vs NHE at pH = 0).

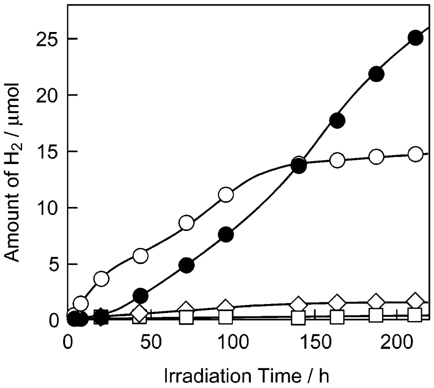

**Figure 3.** Time−course of photoinduced $H_2$ evolution reaction by Pt-loaded HgS (Wako) powders; closed circle, HgS with 2 wt % Pt (photodeposited); open circle, HgS with 2 wt % Pt (sol); diamond, control without HgS and Pt; square, bare HgS.

reaction from aqueous solutions of TEOA. HgS has been reported to be a direct-band-gap semiconductor with band-gap energy in the region of 2.09−2.1 eV at 300 K.[6,13,14] However, the exact positions of conduction and valence band edges are not clear.

To address this problem, the abilities of bare and Pt-loaded HgS inducing $H_2$ evolution under photoirradiation using TEOA as an electron donor were examined. Figure 3 shows yields of $H_2$ from 5 vol % TEOA in the presence Pt-loaded (2 wt %) HgS suspension under deaerated conditions. It was found that the photoirradiated Pt−HgS suspension produced an appreciable amount of $H_2$ compared with that produced in control experimental runs (without the copresence of TEOA, Pt, HgS, and photoirradiation at >300 nm). An appreciable induction period for $H_2$ evolution could be seen in the photodeposited Pt−HgS suspension, as has been also observed for platinized titanium(IV) oxide ($TiO_2$) photocatalysts.[16] The actual rate of $H_2$ evolution estimated from the slope of the time−course curve seemed to be independent of the method of platinization, salting-out from sol or photodeposition, while the estimated rates in the case of prolonged irradiation (>100 h) were different. Although the activity was much lower than those of CdS and ZnS photocatalysts, we could observe photoinduced $H_2$ production from an aqueous solution of TEOA. At present, we cannot conclude the catalytic action (molar yield of the product $H_2$ exceeding the molar amount of HgS, ca. 215 μmol), but assuming the photocatalysis by HgS, it is expected that the edge of the conduction band of HgS is located above (negative to) the $H_2$ evolution and that of the valence band is located below ca. 2 eV of the conduction band, i.e., of oxidation ability a little smaller than that of CdS and ZnS.

**Impurities.** Table 1 shows the results of semiquantitative analysis of several representative HgS specimens. The main impurity elements were sodium, magnesium, aluminum, calcium, titanium, copper, selenium, antimony, and lead. Although we have not determine whether these impurities were incorporated in the cinnabar crystals or in attached independent crystallites, more than 1% impurities were contained in HgS-I. These impurities might give influence on the photoactivity of HgS and will be discussed later.

**Photochemical Reactions of Lysine by HgS Suspension.** It was found that HgS has the ability to produce PCA by photoirradiation of its aqueous suspension containing lysine. The molar amounts of PCA liberated over various natural and synthesized powders after light irradiation at >300 nm are shown in Table 2. Since, in all the cases, the conversion of lysine was too small to be below the experimental error, selectivity of PCA production, a molar ratio of PCA to consumed lysine, was not measured; i.e., mass balance in the HgS-induced photoreaction could not be clarified. It has been reported that photocatalytic reaction by CdS and ZnS produces a cyclic Schiff base intermediate and its ring-opened derivative as byproducts.[17] We also tried to measure the wavelength dependence but failed to obtain with appreciable reproducibility owing to the much slower rate of reaction when irradiated by a mercury arc with optical filters.

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**Table 1.** Results of Semiquantitative Analyses of Representative Natural HgS Samples[a]

| | | content in cinnabar/ppm | | | |
|---|---|---|---|---|---|
| element | detection limit/ppm | FF | G | H | I |
| B | 0.5 | 5 | 5 | 2 | 5 |
| F[b] | 100 | *c* | 0 | *c* | *c* |
| Na | 2 | 50 | 20 | 10 | 500 |
| Mg | 0.05 | 100 | 1000 | 1000 | 5000 |
| Al | 2 | 2 | 0 | 5 | 50 |
| Si[d] | 0.5 | 0 | 0 | 0 | 2 |
| P | 20 | 0 | 20 | 50 | 0 |
| S[e] | 20 | 500 | 500 | 500 | 1000 |
| Cl[b] | 100 | *c* | 0 | *c* | *c* |
| K | 10 | 20 | 0 | 0 | 50 |
| Ca | 0.01 | 100 | 2000 | 2000 | 10000 |
| Ti | 0.3 | 2 | 1 | 10 | 50 |
| Cr | 1 | 2 | 0 | 1 | 1 |
| Mn | 0.3 | 0.5 | 1 | 0 | 5 |
| Fe | 1 | 0 | 0 | 0 | 50 |
| Ni | 2 | 2 | 0 | 2 | 0 |
| Cu | 3 | 50 | 500 | 20 | 0 |
| Zn | 1 | 1 | 5 | 2 | 0 |
| As | 20 | 0 | 20 | 0 | 0 |
| Se[e] | 50 | 0 | 1000 | 100 | 0 |
| Br[b] | 100 | *c* | 0 | *c* | *c* |
| Sr | 0.02 | 5 | 10 | 5 | 5 |
| Mo | 3 | 0 | 0 | 20 | 0 |
| Ag | 1 | 2 | 2 | 2 | 0 |
| Cd | 2 | 20 | 10 | 10 | 10 |
| Sn | 5 | 5 | 0 | 0 | 0 |
| Sb | 10 | 10 | 1000 | 50 | 0 |
| Ba | 0.1 | 1 | 5 | 5 | 1 |
| Pb | 10 | 10 | 500 | 50 | 20 |
| total[f] | | 887.5 | 6599 | 3844 | 16749 |
| rate[g] | | 0.115 | 0.099 | 0.042 | 0.016 |

[a] Powder samples were decomposed by aqua regia, and the filtrate solutions were analyzed by a Perkin-Elmer OPTIMA 3300-DV ICP (inductively coupled plasma) emission spectrometer unless otherwise stated. See Table 2 for the code of HgS samples. The effective figures were in the range 1−1.5. A figure "0" means that the concentration was lower than the detection limit of each element. [b] Analyzed by ion chromatography with a Shimadzu LC-10AD high-performance liquid chromatograph. [c] Not analyzed. [d] The data could be estimated lower due to incomplete dissolution in the acid filtrate. [e] Due to escape from the samples during the aqua regia decomposition process, the data were qualitative. [f] Sum of figures for each sample. [g] Rate of PCA production in the unit of $\mu$mol h$^{-1}$. Data were derived from Table 2.

The PCA yield depended on the kind of HgS sample used, though the rate of PCA formation by HgS was generally much slower than those by ZnS and CdS under similar reaction conditions. Quantum efficiency of PCA production, as a ratio of rate of PCA formation and flux of incident photons of energy greater than the band gap (2.1 and 2.4 eV), by HgS (cinnabar FF in Table 2) and CdS (Table 2) was evaluated roughly to be $1.4 \times 10^{-5}$ and $1.5 \times 10^{-4}$, respectively. The smaller band gap of ca. 2 eV leading to lower oxidation ability, as discussed above, might account for this slower rate. An alternative interpretation of the lower activity of HgS is possible enhanced recombination of photoexcited electron and positive hole at the impurity sites in the crystallites, since the natural specimens of HgS contains appreciable amount of impurities (see Table 1), as well as the small surface area of crashed natural HgS samples (<1 m$^2$ g$^{-1}$; see Table 2). However the synthesized HgS powders, of relatively high purity and large surface area (>5 m$^2$ g$^{-1}$), also showed lower activities and we could not conclude which was the decisive factor for the lower activity of HgS compared with those of CdS and ZnS.

Since the molar amount of PCA did not exceed that of HgS (215 $\mu$mol) in any case, we could not confirm the catalytic action of HgS, but it was clarified that HgS powder induced the photoproduction of PCA from lysine, in a manner[17] similar to that of CdS and ZnS. It should be noted that HgS lumps from various sources (ca. 4−8 mm cubes, twin or single crystals) also gave PCA, suggesting the possibility of the occurrence of a photoinduced reaction by cinnabar in contact with water under solar radiation in ancient times. As can be seen in Table 2, the abilities of the HgS powders studied here were quite different, and these differences were attributable to the differences in surface physicochemical properties, crystallinity, and defect sites in the crystallites. One of the possible reasons of the different photoactivities among natural HgS specimens is impurity included in the crystallites. As shown in Table 1, cinnabar I contains more than 1% impurities and showed the lowest activity for PCA production, while one of the most active specimens, cinnabar FF, was relatively pure. We found that during photoinduced reactions of lysine with HgS (black), the color of the suspension gradually changed from black to red, while that of HgS (red) turned brown. The difference between the activities of the two forms of HgS, black and red, was not so clear, but the higher activity of red HgS was observed[12] by Stephens et al. in the catalytic production of hydrogen peroxide using homemade black and red HgS powders; the activity of the red form was several times larger than that of the black form. Although the yield of PCA contained a large error (ca. 10−20%), especially in such a low yield, indicating that caution is needed in analyzing the results, an interesting finding was that red ($\alpha$) HgS tended to give a small enantiomeric excess (ee) of PCA, while the PCA products from the black ($\beta$) HgS suspensions were almost racemic. This suggests that the chiral $\alpha$-HgS crystallites, not the optically inactive $\beta$-HgS ones, induce the stereoselective production of PCA. However, the synthesized particles of HgS must be optically inactive overall, and if any stereoselections occur, they are canceled. Therefore, we cannot conclude, at this stage, that the chiral HgS gave optically active products under the condition of photoirradiation. The stereoselectivity will be discussed later.

Figure 4 shows the time−course of PCA yield from the natural and commercial powders. In both cases, the PCA formation was appreciable after irradiation of >24 h, and further dramatic increases in PCA yield were seen at ca. 70-h and 100-h irradiation of the natural and commercial samples, respectively. At present, we have no structural evidence, but photoinduced partial decomposition of HgS to give metallic Hg on the surface of particles might account for the enhancement. A similar deposition of cadmium metal on CdS powders has been shown to enhance the photocatalytic activity and control the stereoselectivity of products.[18] The slight change in the appearance of the HgS suspension, from bright red to brownish red, after the induction period may

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**Table 2.** Amounts of Pipecolinic Acid (PCA) Obtained by Photoirradiation (>300 nm) of Deaerated Aqueous Solution of Lysine in the Presence of Suspended or Placed HgS, CdS, and ZnS

| samples$^a$ | appearance$^b$ | irradiation$^c$/h | PCA$^d$/$\mu$mol | ee$^e$/% | OR$^f$/deg |
|---|---|---|---|---|---|
| cinnabar A | crushed SC | 140 | 4.6 | 3 (*S*) | |
| cinnabar A | crushed SC | 144 | 11.9 | 6 (*R*)$^g$ | +0.0008$^g$ |
| cinnabar B | crushed SC | 140 | 4.3 | 2 (*S*) | |
| cinnabar C | crushed SC | 96 | 4.2 | ~0 | |
| cinnabar D | crushed CT | 140 | 7.8 | ~0 | |
| cinnabar E | crushed SC | 96 | 8.8 | 6 (*R*) | |
| cinnabar E | crushed SC | 120 | 4.4 | 4 (*R*) | +0.0022 |
| cinnabar E | crushed SC | 96−120 | 12.0 | 2 (*R*)$^h$ | +0.0019$^i$ |
| cinnabar F | lump CT | 168 | 0.4 | 15 (*S*) | |
| cinnabar FD$^j$ | crushed SC | 120 | 6.8 | ~0 | |
| cinnabar FD$^j$ | crushed SC | 144 | 3.5 | 5 (*S*) | +0.0030 |
| cinnabar FF$^j$ | crushed SC | 120 | 13.8 | 2 (*S*) | |
| cinnabar FG$^j$ | crushed SC | 168 | 4.8 | ~0 | |
| cinnabar G | crushed SC | 96 | 9.5 | ~0 | |
| cinnabar H | crushed SC | 200 | 8.3 | 3 (*S*) | |
| cinnabar I | crushed SC | 140 | 2.3 | 7 (*S*) | |
| cinnabar I | crushed SC | 168 | 0.8 | 18 (*S*) | +0.0006 |
| cinnabar I | lump SC | 336 | 0.5 | 6 (*S*) | |
| cinnabar I | lump SC$^k$ | 530 | 0.8 | 14 (*R*)$^l$ | +0.0039$^m$ |
| Strem | Brown-red G | 144 | 4.0 | ~0 | |
| Wako | red FP | 168 | 1.9 | 5 (*S*) | |
| Wako | red FP$^n$ | 168 | 3.4 | 8 (*S*) | |
| Mitsuwa | red FP | 144 | 3.4 | 4 (*S*) | |
| Kanto | red FP | 144 | 1.1 | 2 (*S*) | |
| Nacalai | red FP | 144 | 1.8 | 4 (*R*) | |
| High Purity | red FP | 144 | 3.9 | 7 (*S*) | |
| High Purity | black G | 144 | 2.2 | ~0 | |
| Aldrich | red FP | 96 | 0.3 | 11 (*R*) | |
| Aldrich | black G | 144 | 4.0 | ~0 | |
| CdS (Katayama) | red FP | 24 | 13.9 | ~0 | |
| ZnS (Nacalai) | white FP | 24 | 13.2 | ~0 | |

[a] Cinnabar A−C crystals were obtained from Switzerland, D and E from Hunan province, China, and F−I from Guizhou Province, China. BET surfaced areas of cinnabar FD and G were 0.2 and 0.7 $m^2\ g^{-1}$, respectively. [b] SC: single crystal. CT: crystal twin. G: grain. FP: fine powder. [c] Irradiation of light with a wavelength of >300 nm was performed at 298 K under Ar with magnetic stirring (1000 rpm). [d] Total molar amount of (*R*)- and (*S*)-pipecolinic acid (PCA). [e] Enantioexcess % of PCA evaluated by HPLC analysis. “*R*” and “*S*” in parentheses show the configuration of PCA, (*R*) and (*S*), respectively. [f] Optical rotation of the reaction mixture after centrifugation and filtering (0.1 $\mu$m). [g] The corresponding CD spectrum is shown in Figure 6a suggesting 82% ee (*R*). [h] CD spectrum (Figure 6b) suggested 43% ee (*R*). [i] OR was measured after ion-exchange resin (IRC-50) separation of mixed four reaction samples followed by dilution to 20 $cm^3$ (5 $cm^3$ × 4) (CD: Figure 6b). [j] Cinnabar FD, FF, and FG were collected from one specimen of a cinnabar sample. [k] Treated with aqua regia before reaction. [l] CD spectrum (Figure 6c) suggested 34% ee (*S*). [m] OR was measured after TLC separation of the original reaction solution with 2.5× concentration (2 $cm^3$) (CD: Figure 6c). [n] 0.5 wt % $Hg^{2+}$ (as $HgCl_2$) was added.

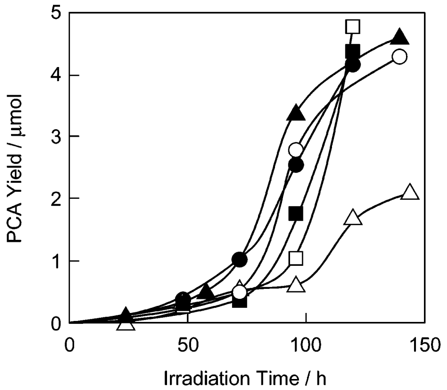

**Figure 4.** Time−course of photoinduced PCA formation from lysine in deaerated aqueous suspensions of HgS: open circle, cinnabar B; closed circle, cinnabar C; open square, cinnabar D; closed square, cinnabar E; open triangle, Wako HgS; closed triangle, cinnabar A.

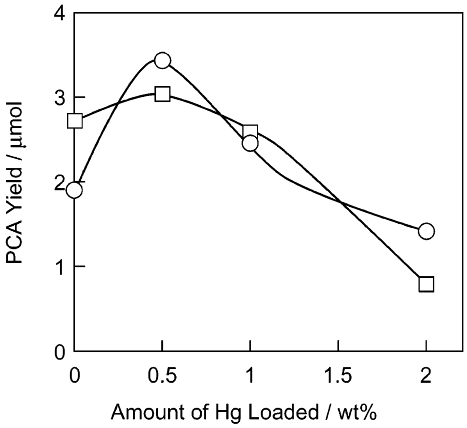

**Figure 5.** Effect of Hg loading on PCA formation over HgS (Wako) powder: circle, irradiation for 168 h; square, irradiation for 192 h.

support this speculation. The fact that hydrogen sulfide ($H_2S$) was liberated, as detected by its characteristic smell but not measured quantitatively, is evidence of partial decomposition of HgS. On the basis of the assumption of a reaction mechanism including Hg metal deposition, the different activities of HgS samples are attributed to different surface and bulk structures, e.g., defective sites, as have been proposed for CdS photocatalysts to lead to the deposition. Addition of a small amount of $Hg^{2+}$ (as chloride, Table 2) doubled the PCA yield with HgS (Wako) of rather poor activity. This observation is further supported by the reactions of different (0−5 wt %) Hg-loaded HgS (Wako) powders for the enhancement of PCA production. Figure 5 shows the effect of Hg loading. We performed two sets of experiments with Hg-loaded HgS (Wako) powders, and it was found that 0.5 wt % Hg loading gives the highest PCA yield, which gradually decreases with further increases in Hg loading. Since photoreduction of $Hg^{2+}$ to Hg over $TiO_2$ has been reported,[19] this improvement is attributed to the acceleration by deposited Hg metal. The amount of deposited Hg during the course of photoreaction could not be measured, mainly due the difficulty in analyses of air-sensitive Hg deposits, and therefore, we have no quantitative interpretation on the change of rate during the course of photoreaction shown in Figure 4.

As has been reported previously, when optically active L-(*S*)-lysine was used as a substrate for the photocatalytic reaction, titanium(IV) oxide ($TiO_2$) gave L-(*S*)-excess PCA, while CdS and ZnS induced the formation of an almost racemic product.[17,20] This reaction has been shown[2,17,20] to proceed via three reaction steps, including both oxidation and reduction. Lysine undergoes deaminocyclization through (1) oxidation of an amino group by positive holes to yield an imine, (2) hydrolysis of the imine into aldehyde (or ketone) and ammonia and intramolecular condensation with a remaining amino group, and (3) reduction by photoexcited electrons, presumably on the deposited Hg surface, of the resulting Schiff base intermediate. The product selectivity has been proved to be determined by the difference in positions of lysine to be oxidized by photogenerated positive holes (Scheme 1); oxidation at the α-amino moiety leads to the formation of a racemic product. In the present HgS system, almost racemic PCA was obtained from (*S*)-lysine, indicating that an α-amino group is oxidized in the first step of positive-hole oxidation. The selective oxidation at the α-amino group in lysine by CdS has been attributed to feasible oxidation of its deprotonated form in the aqueous solution rather than the protonated terminal amino group and to the lower oxidation ability of CdS, which is not sufficient to oxidize the protonated amino group.[20] This may also be the case for HgS as discussed earlier.

We investigated mainly racemic DL-(*R*,*S*)-lysine as a starting amino acid in test reactions. If the stereoselective oxidation occurs in the first step on the chiral HgS surfaces, we can expect the remaining lysine to have optical activity (Scheme 1, checkpoint 1). Similarly, if the product, PCA, is produced enantioselectively in the final step, PCA would have optical activity (Scheme 1, checkpoint 2). As shown in Table 2, we could detect little ee of PCA that was almost within the experimental error with less reproducibility. To clarify this point, a sample of the reaction mixtures was purified by ion exchange chromatography. CD spectra of the part of reaction mixture that was expected to contain PCA but not lysine are shown in Figure 6. Characteristic spectra similar to the authentic PCA could be observed, but the ee % estimated from a comparison of the authentic spectrum was much larger than or opposite to that expected from the HPLC analyses, as shown in Table 2. Therefore, we concluded that these CD spectra might be due to some impurities, not due to enantioselective formation of PCA.

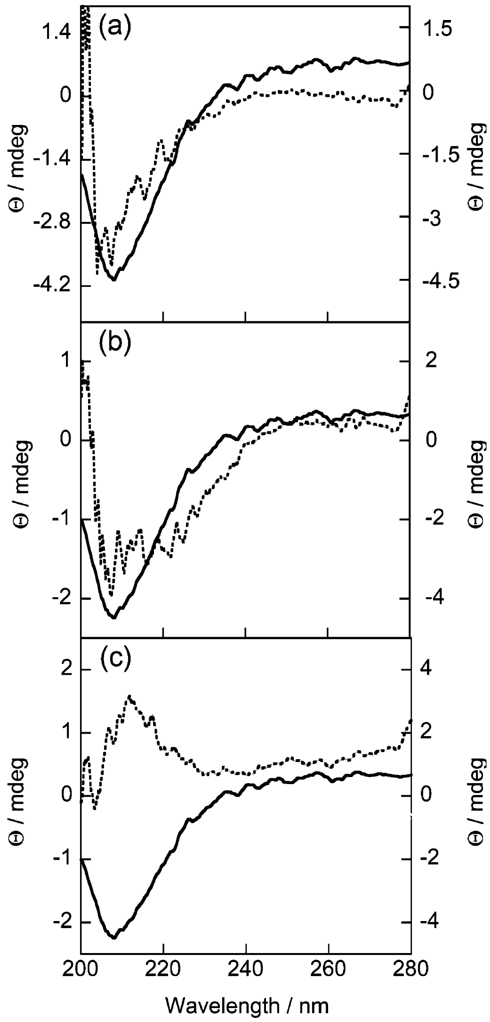

**Figure 6.** CD spectra of three HgS-mediated reaction solutions: (a) original reaction solution of cinnabar A after 144 h of irradiation (dotted line, entry in Table 2); (b) after the ion-exchange resin separation of mixed four reaction solutions (dotted line, entry in Table 2, cinnabar E, 96−120 h of irradiation; only the PCA part containing a trace amount of lysine and other impurities); (c) after TLC treatment of cinnabar I lump reaction solution after 530 h of irradiation (dotted line, entry in Table 2; only the pure PCA part containing negligible amounts of other products). Solid lines in (a)−(c) are of 0.2 mmol $dm^{-3}$ (*R*)-PCA.

On the basis of the speculation that the final reduction step for the cyclic Schiff base intermediate occurs on the surface of deposited Hg through electron transfer, not on the HgS surface, the effect of the chiral crystal structure of HgS on the enantiomeric excess of PCA should not be expected. This means a rather unfavorable situation; if some stereoselective oxidation occurs at the first step, this should be on the α-position to give an optically inactive Schiff base intermediate; i.e., we cannot check whether the stereoselective oxidation occurs at the first step from the optical activity of product PCA. On the other hand, measurement of the optical activity of the remaining lysine must be of great significance, since this shows the stereoselections at the first oxidation step directly. However, due to the much lower conversion of lysine by the photoinduced reaction of HgS suspensions, the asymmetric consumption of lysine could not be differentiated from optical activity measurement.

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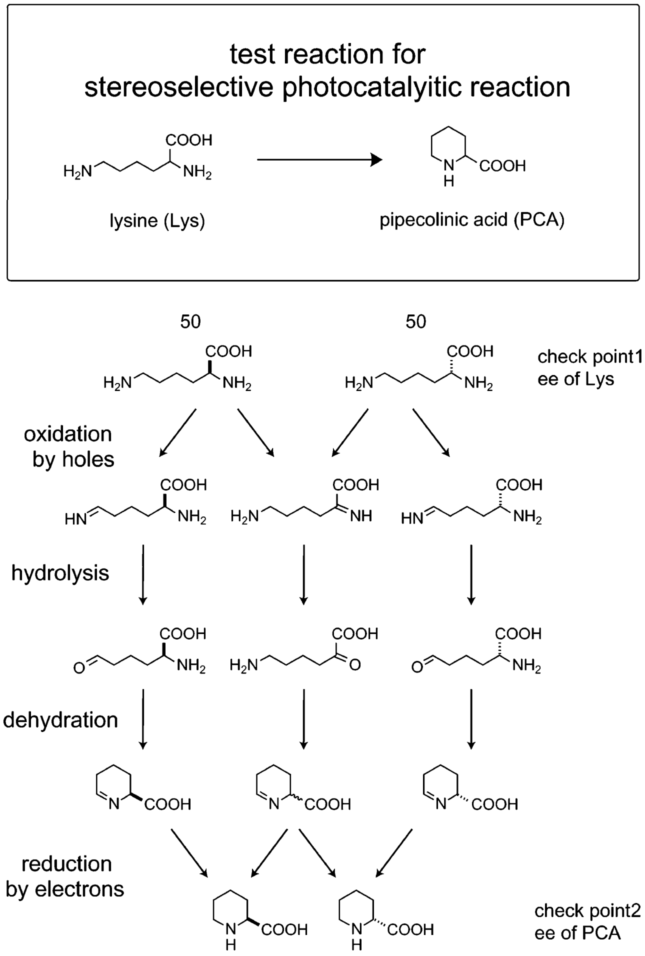
**Scheme 1.** Proposed Reaction Mechanism of Photoinduced Conversion of Lysine into PCA



**Adsorption Effects and Plausible Optical Activity.** Since it has been reported[21,22] that optically active quartz crystals are capable of adsorbing optical enantiomers to different extents, we investigated the adsorption effects of (*R*)-, (*S*)-, and racemic lysine as starting substrates on the product PCA selectivity over HgS crystal surfaces. However, due to the very low concentrations of the adsorbed substrates, we could not differentiate any asymmetric bias in the adsorption process by HPLC. With this in mind, we investigated the effect of the starting substrate on the PCA yield under the same experimental conditions. Figure 7 shows the yield of PCA after 144-h irradiation. It can be seen that there was always a difference among the PCA yields by each HgS powder. There was a significant difference in the PCA yields over a natural single crystal (cinnabar E); the PCA yield from (*S*)-lysine was much larger than that from (*R*)-lysine, though a relatively small but appreciable ratio was also observed in the case of commercial synthesized HgS powders. The implications of such observations may constitute a valid demonstration of the ability of chiral HgS to adsorb optically active substrates asymmetrically, which in turn might change the product (PCA) selectivity during photoinduced reactions. However, again, a conclusion on this could not be made.

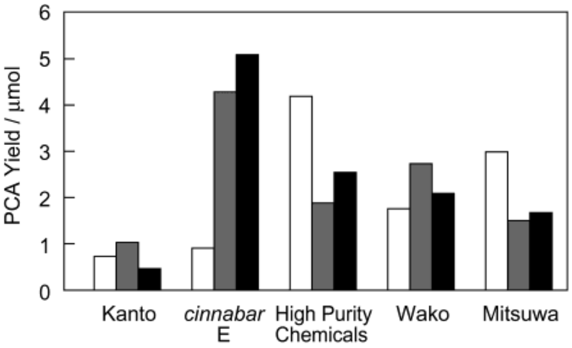


**Figure 7.** Effect of the nature of the starting substrate, lysine, on the PCA yield. Open, shaded, and closed bars show the results when (*R*)-, (*R*,*S*)-, and (*S*)-lysine were used, respectively.

## Conclusions

We have clarified that natural and commercial HgS crystals sensitize the photoinduced conversion of lysine to PCA, presumably via a redox combined mechanism similar to that observed for the CdS or ZnS photocatalyzed reaction. This is the first example, to the best of our knowledge, of photoinduced reaction of naturally occurring amino acid on the surface of natural minerals, suggesting the possibility of such solar chemical reactions having occurred in ancient times (and, of course, occurring now). The photoirradiation induced the decomposition of HgS along with the formation of $H_2S$ and the deposition of Hg metal, which might play a role as a reduction site for the cyclic Schiff intermediate. The rates of PCA formation by HgS suspensions were rather small compared with those by CdS and ZnS. It is thought that the chiral crystal structure of HgS induces stereoselective conversion of lysine to PCA, but we could not obtain evidence of this due to the much lower rate of photoinduced reaction to give appreciable difference in enantiomeric yield of PCA and catalysis of the deposited Hg metal in the reduction step, presumably without enantioselection. Since the synthesized HgS powder is expected to be optically inactive overall and natural mineral specimens of cinnabar, though they are optically active single crystals, contain impurities reducing the photosensitizing activity of HgS, studies using synthesized large-sized single crystals are needed. Further investigation along this line is under way.

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