J. Am. Chem. Soc. 1981, 103, 6893–6897

protons and no methyl groups. The exact position of the methyl groups cannot be determined from these experiments but it is safe to assume that during the initial rearrangement reaction (k_{12} in Scheme I) a hydrogen migrates and not a methyl group. This hydrogen shift at low temperatures is one of the most interesting aspects of the photoreactions of A and, especially, TMA. The very small and apparently temperature dependent activation energy (cf. Figure 3a) in the case of TMA indicates that a tunneling process may become important. Steady state experiments designed to isolate the primary rearrangement product and kinetic experiments carried out at temperatures below 77 K with deuterated and undeuterated TMA are in progress.[8] In the case of A, the disproportionation reaction 2DHC $\rightarrow$ C + THC is predominant which makes the determination of k_{12} and the structure analysis of the rearrangement product extremely difficult.

Experimental Section

Materials. *N*-Methyldiphenylamine (Eastman-Kodak, Anal. Grade) was purified by several distillations until the purity was >99.99% (determined by GC).

***N*-Methyl-1,3,5,1′,3′,5′-hexadeuteriodiphenylamine** (Merck, Sharp and Dohme) was used without further purification (isotopic purity 90 atom % D, by MS).

***N*-Methyl-2,4,6-trimethyldiphenylamine.** 2,4,6-Trimethylacetanilide (84.5 g, 0.5 mol) and 264 mL (2.4 mol) of iodobenzene were suspended in 380 mL of dry nitrobenzene and 181 g (1.1 mol) of K_2CO_3 and 3 g of freshly precipitated and washed (dry ether) Cu were added. The mixture was refluxed under stirring for 48 h at 200 °C. The suspension was filtered, with 1.5 L $CHCl_3$ extracted, the solvent evaporated, and the residue chromatographed on Al_2O_3 with cyclohexane–ether 1:1; yield 3.67 g (2.9%) *N*-acetyl-2,4,6-trimethyldiphenylamine; mp 109.1 °C; IR (KBr) 1670 cm^{-1} (CO). Hydrolysis with KOH in triethylene glycol (24 h under reflux) yielded 2.6 g (70%) of 2,4,6-trimethyldiphenylamine which was recrystallized from 2-methylbutane as white crystals; mp 56.6 °C; UV_{max} (log ϵ) in methylcyclohexane 264 (3.90) and 241 (4.07) nm; IR (KBr) 3385 cm^{-1} (NH); NMR ($CDCl_3$) 2.2 (6 H, singlet), 2.3 (3 H, singlet), 5.1 (1 H, singlet), 6.4–7.3 (7 H, multiplet); anal. found (calcd) C 85.1 (85.3), H 8.21 (8.05), N 6.47 (6.63). One gram (0.005 mol) of 2,4,6-trimethyldiphenylamine and 2 g (0.014 mol) of trimethyl phosphate were very slowly heated (fuming has to be avoided) to 200 °C under N_2 and stirred for 3 h. After cooling 100 mL of NaOH (13%) were added, the mixture refluxed for 2.5 h under N_2, the solution extracted with ether, and the extract dried with Na_2SO_4 and evaporated. The residue was chromatographed on Al_2O_3 with cyclohexane–CCl_4 1:1 and further purified with preparative GC (1.72 m column, i.d. 25 mm, 5% silicone rubber SE 52 on Celite 60–100 mesh, gas flow rate 1200 mL/min, column temp. 180 °C); yield, 0.2 g (20%) *N*-methyl-2,4,6-trimethyldiphenylamine; white crystals; mp 26 °C; UV_{max} (log ϵ) in methylcyclohexane 310 (3.43), 283 (3.75), 247 (4.27) nm; NMR ($CDCl_3$) 2.1 (6 H, singlet), 2.35 (3 H, singlet), 3.2 (3 H, singlet), 6.3–7.3 (7 H, multiplet).

Solvents. Methylcyclohexane (Baker) and 2-methylbutane (Baker) were distilled and chromatographed.[13] Decalin (Baker) was diluted by 2-methylpentane (1:1), chromatographed, and separated thereafter from 2-methylpentane by distillation.

Irradiation. Spectroscopic irradiations were performed with about 5 × 10^{-5} M solutions of the amines in 1 × 1 cm^2 quartz cells with MCH as solvent. The solutions were degassed on a high vacuum line, using the freeze–pump–thaw technique, and sealed off. The cooling technique of Fischer[14] was applied for irradiations at low temperatures. Preparative irradiations of A and A_d were performed in a thermostated 1 L Pyrex vessel. A medium pressure Hg lamp (Quartzlampenges. Hanau, Model TQ 150) was placed inside the vessel, separated from the solution by a filter liquid (0.1 g/L of $K_2Cr_2O_4$ and 140 g/L of $CoSO_4{\cdot}7H_2O$ in water, thickness 1 cm, transparent for 313 nm) and a vacuum mantle. TMA solutions were placed in a quartz vessel and illuminated at 254 nm with a Rayonet RPR 100 reactor. A styrofoam Dewar with four 20 cm long quartz windows made of evacuated quartz tubing with rectangular cross section (4 × 15 mm^2) surrounded the quartz vessel which was cooled with a thermocouple-controlled stream of liquid nitrogen. The extent of the reaction was controlled by measuring the UV spectra of small samples taken from the solution. During the irradiation the solutions were bubbled with nitrogen. After irradiation the solvent was partly evaporated at room temperature with a stream of nitrogen. The concentration of the solutions was 10^{-3} M and the volume was 600–800 mL.

Separation of Reaction Products. The volume of the irradiated solutions of A and of A_d was reduced to 100 mL as described above and treated with concentrated HCl. C and *N*-methyl-1,3,6,8-tetradeuteriocarbazole remained in the organic phase. After fourfold dilution of the HCl phase with water the other reaction products precipitated. The dihydrocarbazoles formed from TMA were isolated by means of preparative GC (see under *N*-methyl-2,4,6-trimethyldiphenylamine for conditions).

Spectra. UV spectra were recorded on a Cary 17 and IR spectra on a Perkin-Elmer Model 257 recording spectrophotometer. Mass spectra were measured on a Varian MAT Model CH 7 instrument at 70 eV and NMR spectra on a Varian T 60 (60 MHz) or on a Bruker WH 270 pulse fourier transform (270 MHz) instrument. For analytical gas chromatography a Perkin-Elmer Model F 7 and for preparative gas chromatography a Perkin-Elmer Model F 21 chromatograph were used.

Flash Photolysis. The flash apparatus has been described elsewhere.[2m] Solutions (1 × 10^{-4} M) of the amines in MCH were degassed and cooled as described above for spectroscopic irradiation.

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[13] Kühnle, W., Woelm Information 5a.

[14] Fischer, E. *Mol. Photochem.* **1970**, *2*, 99–102.

Heterogeneous Photosynthetic Production of Amino Acids at Pt/TiO_2 Suspensions by Near Ultraviolet Light

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Abstract: Studies of the previously reported production of amino acids (glycine, alanine, serine, aspartic acid, glutamic acid) from methane, ammonia, and water in contact with irradiated suspensions of Pt/TiO_2 were extended. Products were analyzed by LC, HPLC, and coupled GC/mass spectroscopy. Analysis of product mixtures also shows the presence of MeOH, EtOH, and CH_3NH_2 as products of the photoprocess. Experiments with nitrogen-15 labeled ammonia showed that the nitrogen in the amino acids originated with the NH_3 rather than from contaminants. Amino acids were also produced from the CH_4–NH_3–H_2O mixture during decomposition of hydrogen peroxide at Pt foil. A mechanism for the reaction based on free-radical reactions initiated by hydroxyl radical produced at the irradiated catalyst is proposed.

A previous communication from this laboratory[1] described the production of amino acids by xenon lamp irradiation of platinized TiO_2 powders (Pt/TiO_2) suspended in aqueous ammoniacal solutions saturated with methane. The process apparently occurs by a photosynthetic (energetically uphill) reaction driven by the absorption of the near-ultraviolet (λ <405 nm) radiation by the TiO_2. These reaction conditions for amino acid formation from a simple reducing mixture are mild compared to previous methods for amino acid production that involved electrical discharge or very short wavelength radiation.[2]

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[1] Reiche, H.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 3127.

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The proposed reaction mechanism is analogous to other heterogeneous photoprocesses at semiconductor materials.[3,4] Irradiation of the semiconductor with energy greater than that of the band gap produces an electron/hole pair. The holes can oxidize species at the semiconductor surface; for example, irradiation of Pt/TiO_2 was shown to produce hydroxyl radicals.[5] The electrons cause a reduction reaction at the particle surface. In many cases the deposition of Pt on the semiconductor increases the rate of the photoreaction by catalyzing (i.e., reducing the overpotential for) the reduction reaction.

We present here a more detailed examination of the production of amino acids on Pt/TiO_2 and demonstrate production under actual solar, as well as xenon lamp, irradiation. Mass spectral identification of the products and experiments employing isotopically labeled ammonia ($^{15}NH_3$) are reported. Parallel experiments demonstrating amino acid production by chemically produced hydroxyl radicals in similar systems permit us to propose a tentative mechanism for the reaction at the illuminated powder.

Experimental Section

Chemicals. The TiO_2 powder was purchased from Matheson, Coleman, and Bell (MCB) in the anatase form. The X-ray diffraction spectra showed the characteristic anatase peak at 25.2° 2θ (3.52 Å); the principal rutile peak at 27.3° 2θ (3.25 Å) was absent.[6] The surface area, measured by the B.E.T. (Micrometrics Model 2100 B, Surface Area—Pore Volume Analyzer) method was approximately 15 m^2/g. The powders were reduced at 500 °C in a H_2 atmosphere for 8 h. Platinum was photodeposited on the TiO_2 surface by the photocatalytic reduction method previously described.[7] The catalysts contained about 10% Pt by weight. All photocatalysts were washed repeatedly with distilled water prior to use. The 2 M NH_3 (MCB, 28%) and NH_4Cl (MCB, fused) were prepared from reagent grade chemicals. The methane gas (Big 3 Industries, 99%) was passed through saturated $Ba(OH)_2$ to remove CO_2 (as $BaCO_3$), and in a few experiments also through a reductor containing 1 M $Cr(NO_3)_3$ in contact with Zn(Hg) placed before the sample cell to remove trace O_2 from the methane gas. A second $Ba(OH)_2$ trap was placed after the reaction cell to prevent any back-diffusion of CO_2 into the system. Methanol (MCB, Omnisolve) and 95% ethanol were used as alternative carbon sources. Labeled ammonium chloride ($^{15}NH_4Cl$, 99%) was obtained from KOR, Inc. (Cambridge, Mass.).

Reaction Procedures. Photocatalytic experiments were conducted in a one-compartment Pyrex cell having a flat window for illumination. In order to remove infrared radiation the reaction cell was immersed in a large Pyrex water bath. The bath was equipped with a water-cooling coil to maintain the cell temperature at 27 ± 4 °C. The illumination source was a 2.5 kW xenon lamp (Christie Corp., Los Angeles, CA, Model UF 30 KK) operated at 1.6 kW. The focused intensity on the cell was about 2.5 W/cm^2.

In a typical experiment 250 mg of the Pt/TiO_2 catalyst was suspended in 30 mL of 2 M NH_3 or NH_4Cl. Prior to irradiation, a small aliquot of the reaction mixture was removed for amino acid analysis as a control. The sample solution was bubbled with methane prior to illumination and throughout the reaction period. Following irradiation the powder catalyst was allowed to settle and the solution removed.

Experiments involving isotopically labeled ammonia were carried out in an identical manner, except that solutions were prepared with $^{15}NH_4Cl$. In solar irradiation experiments, a large Pyrex flask with a liquid surface area of approximately 700 cm^2 was employed. In the experiments, 2.4 g of the Pt/TiO_2 catalyst was suspended in 2 L of 2 M NH_4Cl and the experiment carried out for 13 days.

Experiments with Fe_2O_3 (Fischer Scientific) employed 250 mg of the catalyst. Experiments with naturally occurring ilmenite, $FeTiO_3$ (David New Minerals, Stevensville, MT), used 300 mg of the ground crystalline material. The photocatalytic experiments were carried out in a manner identical with those described for Pt/TiO_2. Control experiments to confirm the purity of starting materials were routinely conducted. All glassware was rigorously cleaned and carefully rinsed with distilled water prior to use.

Experiments involving chemical production of hydroxyl radical utilized decomposition of H_2O_2 at a bright platinum foil (area, 5 cm^2). A 2 M NH_3 solution (30 mL) was saturated with methane, the Pt foil was immersed in the solution, and 1-mL additions of 30% H_2O_3 were made at regular intervals over 48 h, until the total solution volume attained 60 mL. Methane was bubbled through the reaction mixture throughout the experiment. An identical experiment was carried out with ethanol, rather than methane, as the carbon source.

Analysis. A 5- to 10-mL portion of the solution after reaction was evaporated to dryness for removal of NH_3. Experiments employing NH_4Cl required the repeated addition of NaOH solution to liberate NH_3, followed by successive evaporation. Routine analysis for amino acids was conducted with a Beckman Amino Acid Analyzer, Model 120C. High-performance liquid chromatography (HPLC) was carried out on a Perkin Elmer (PE) Series 2 dual pump apparatus equipped with a PE LC-65T UV-vis detector. Phenylthiohydantoin (PTH) derivatives (λ_{max} = 254) were separated on a C_{18} reverse phase (PE ODS-HCSIL-X-1) column with use of a methanol/acetate (pH 4) gradient.[8]

Mass spectroscopy was performed with use of a Finnigan Model 2000 EI-CI GasChrom/mass spectrometer. Both PTH derivatives and *N*-trifluoroacylmethyl ester derivatives were used for mass analysis. The PTH derivatives were separated on an OV-1 column (1 m, Suppelco, Inc.). PTH-amino acid standards obtained from Pierce Chemical Co. (Rockford, IL) were used to determine retention times and the mass spectra of the derivatives. Glycine, alanine, and serine could be used in gas chromatography as received. Aspartic and glutamic acids required silation prior to gas-chromatographic determination. Derivatives of the isotopically labeled amino acids were characterized by unit mass shifts in the ion peaks corresponding to the presence of the heavier nitrogen isotope. The acyl ester derivatives were separated on an OV-17 column (1 m, Suppelco, Inc.). A sample containing standard amino acids (Pierce Chemical Co.) was derivatized along with the reaction product sample to determine standard retention times and mass spectra.

The PTH derivatives and *N*-trifluoroacylmethyl esters were prepared by standard methods;[9] experimental details are given by Dunn.[10]

Intermediate Identification. For separation of primary amine intermediates the pH of the reaction mixture was raised to 12 and the first distillation fraction collected. The low concentration of the amine required repetition of the distillation procedure by allowing the product mixture to cool and again raising the temperature. A 1.6-m carbowax column (10%) washed with 8% KOH was used for separation of the amine from NH_3 at −10 °C. Under these conditions the amine was not completely separated from the NH_3. However, by monitoring the principal mass peaks in the primary amine spectrum (*m/e* 28, 30, 31) during GC/mass spectroscopy, the amine was detected near the end of the NH_3 elution region.

In order to analyze for alcohol intermediates in the product mixture, the solution was acidified (converting the NH_3 to NH_4Cl) and the first distillation fraction (92–95 °C) was collected for analysis. GC/mass spectroscopic analysis was performed with use of a carbowax column (10%) to separate the alcohols with the column chamber cooled to −10 °C. Methanol (*m/e* 31) and ethanol (*m/e* 45) were identified by their respective mass spectra.

Results

Photosynthetic Amino Acid Production. The results of amino acid synthesis experiments carried out with irradiation by a xenon lamp and by natural sunlight are given in Table I. The yields reported were determined by comparisons of liquid chromatography results obtained with experimental samples to results obtained with standard amino acid mixtures. A representative set of experimental data is shown in Figure 1. Product analysis was also performed with use of HPLC separation of the amino acids as their PTH derivatives.

Product mixtures routinely contained glycine (Gly), alanine (Ala), serine (Ser), and aspartic acid (Asp). Glutamic acid (Glu) was a less common product. The presence of very small amounts of threonine was indicated in some experimental results obtained

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[2] See, e.g.: (a) Miller, S.; Urey, H. C. *Science* **1959**, *130*, 245. (b) Fox, S. W.; Dose, K. "Molecular Evolution and the Origins of Life"; Marcel Dekker: New York, 1977; Chapter 4 and references therein.

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[5] Jaeger, C.; Bard, A. J. *J. Phys. Chem.* **1979**, *83*, 3146.

[6] X-ray data files, American Society for Testing Materials, Philadelphia, Penn., 1958, No. 21-1272 (anatase); No. 21-1276 (rutile).

[7] Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4317.

[8] Elion, J.; Downing, M.; Mann, K. *J. Chromatogr.* **1978**, *155*, 436.

[9] (a) Blackburn, S. "Amino Acid Determination"; Marcel Dekker: New York, 1968. (b) Caprioli, R. M.; Seifert, W. E. *Biochem. Biophys. Res. Commun.* **1975**, *64*, 295.

[10] Dunn, W. Ph.D. Dissertation, The University of Texas at Austin, 1981.

Table I. Photosynthetic Amino Acid Experiments[a]

expt no.	solution	catalyst	irrad. time, h	total yield, nmol	relative amounts Asp	Ser	Glu	Gly	Ala
1	NH_4Cl	Pt/TiO_2	72	472	0.03	0.98		1.0	
2		Pt/TiO_2	72	353	0.60	0.56	0.73	1.0	0.23
3		Pt/TiO_2	96	50	0.50	1.3		1.0	0.16
4		Pt/TiO_2	88[b]	112	0.10	0.13		1.0	0.20
5		Pt/TiO_2	312[c]	2140	<0.01	<0.01	<0.01	1.0	0.05
6		none	72	0					
7		Pt/TiO_2	0[d]	0					
8		Pt/TiO_2[e]	72	0					
9		Pt/TiO_2[f]	120	382	0.19	0.12	0.05	1.0	
10		Pt/TiO_2[g]	72	41	0.15	1.05	1.15	1.0	0.70
11		Pt/TiO_2[h]	88	90	0.10	<0.01		1.0	0.20
12		Fe_2O_3	88	0					
13		$FeTiO_3$[i]	120	0					
14	NH_3	Pt/TiO_2	88	71	0.74	0.58		1.0	0.37
15		Pt/TiO_2	216	678	0.51	0.17	0.1	1.0	0.30
16		Pt/TiO_2[j]	120	157	0.60	1.04		1.0	0.05
17		Pt/TiO_2	96	46	0.50	2.2		1.0	0.90
18		none	72	0					
19		Fe_2O_3	72	0					
20		TiO_2	0	0					

[a] Unless noted otherwise, 30 mL solution saturated with methane was employed with xenon lamp irradiation. Analysis by Beckman Model 120 C amino acid analyzer. [b] Product analysis conducted with PTH derivatives by HPLC. [c] Solar experiment; solution exposed in Austin, Texas, on January 8-21, 1978. [d] No irradiation, system mixed for 88 h, then analyzed. [e] No methane saturation. [f] EtOH substituted for methane as carbon source. [g] MeOH substituted for methane as carbon source. [h] $^{15}NH_4Cl$ experiment, analysis by HPLC. [i] Mineral ilmenite. [j] Recycled Pt/TiO_2 catalyst used.

with the amino acid analyzer; however, the production of threonine was not confirmed by other techniques.

Several control experiments were performed to ensure that the amino acids were actually produced in the photosynthetic experiments and did not arise from contamination. Experiments without the Pt/TiO_2 photocatalyst (Table I, entries 6 and 18) produced no detectable levels of amino acids. If the system components were combined and not illuminated, no amino acids were produced.

In order to verify that the amino acids produced did not originate with surface carbon on the prepared Pt/TiO_2, recycled catalyst was employed. The catalyst used in experiment 3 was removed, washed repeatedly with distilled H_2O, and dried prior to use. The reaction produced amino acids in yields that were comparable to those produced with freshly prepared photocatalysts (Table I, entry 16). In addition to these controls, numerous control experiments were performed to confirm the purity of starting materials.

In order to investigate the activity of naturally occurring materials for the process, TiO_2, Fe_2O_3, and $FeTiO_3$ (as the ore, ilmenite) were examined as photocatalysts. If the TiO_2 was not platinized, no detectable levels of amino acids were produced in the photoreaction. This lower efficiency of the unmetallized powder may be attributed to the lack of a site for reduction (e.g., of water) on the metal oxide surface. It is known from previous heterogeneous photocatalysis experiments that the presence of platinum lowers the overpotential for proton reduction at the particle surface, thus increasing the catalytic efficiency.[4] Irradiation of an Fe_2O_3 suspension failed to produce any detectable levels of amino acids. Ilmenite, a naturally occurring mixed oxide of Fe and Ti, was also ineffective as a photocatalyst for the process. While these experiments are disappointing in that they fail to show the applicability of unplatinized materials as photocatalysts, they do help confirm that the detected amino acids do not arise as contaminants on the powders.

Note also that more oxidized forms of carbon, such as methanol and ethanol rather than methane (Table I, entries 9 and 10), can serve as sources of carbon. The product ratios of amino acid with these are different than with methane, but the yields appear comparable.

Other Products. In the production of amino acids from CH_4, NH_3, and H_2O in the photosynthetic reaction, other products that behave as intermediates in the later steps should be produced. Indeed, analysis of the product solutions by GC/mass spectroscopy showed the presence of methanol and ethanol. As shown above, these materials can act as carbon sources in amino acid production. Trace amounts of methyl amine were also found in the product mixture by GC/mass spectroscopy.

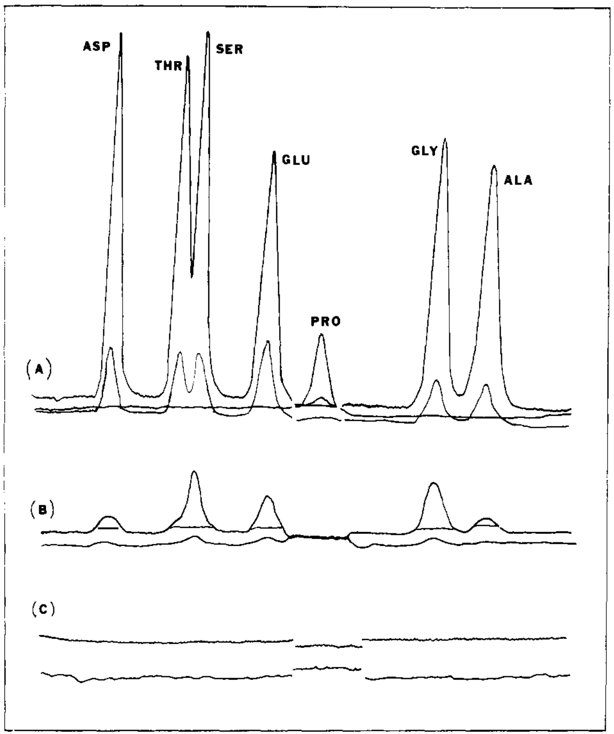

Figure 1. Output from amino acid analyzer for (a) a standard mixture of biological amino acids (33 nmol each), (b) the product of the photosynthetic experiment (see Experimental Section for details), (c) and an aliquot removed from the reaction cell prior to illumination (control sample).

GC/Mass Spectroscopy Results. In order to confirm the identity of the amino acids produced, volatile derivatives of the reaction products were prepared and analyzed by GC/mass spectroscopy. Two different derivatives were chosen for this study: the phenylthiohydantoin (PTH) derivatives and *N*-trifluoroacylmethyl esters. Glycine, alanine, aspartic acid, and serine were identified

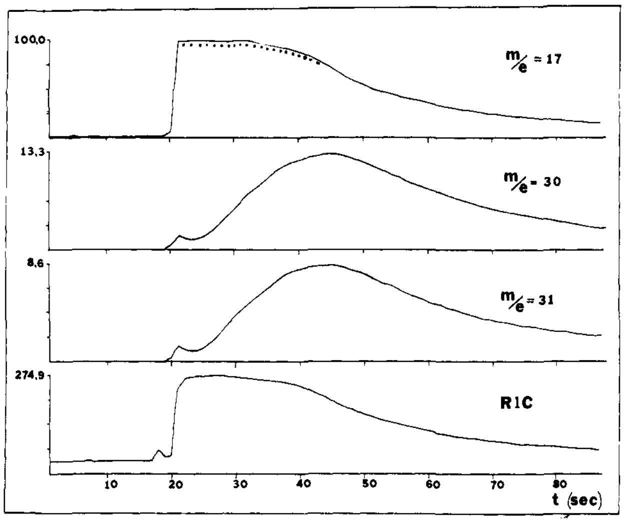

Figure 2. Ion current for methylamine in aqueous NH_3 obtained with GC/MS. (See Experimental Section for details.) Upper chromatogram shows NH_3 elution (*m*/*e* 17, ···· denotes saturated signal). Two center chromatograms are major ion peaks for methylamine (see Figure 3). Bottom chromatogram is the reconstructed ion current (RIC) of the sample.

in the product solutions by comparisons of their mass spectra and retention times to those of prepared standards. No derivatives of glutamic acid were detected in the product mixture, apparently because its concentration was too low to be found by this method. The mass spectra obtained for the photoreaction products positively identify the products as the amino acids, thus eliminating the possibility that the reaction products are other compounds with identical elution times in the liquid chromatography analysis.

Amino Acid Production with Isotopically Labeled $^{15}NH_3$. In order to verify that the nitrogen source in the amino acids photochemically produced was the NH_3 and not, for example, organic contaminants, experiments were conducted with use of nitrogen-15 labeled NH_4Cl. The reaction conditions were identical with those of other photosynthetic experiments. PTH derivatives were prepared from the products by the standard method, and those were analyzed by GC/mass spectroscopy. Alanine and glycine containing ^{15}N-labeled amine groups were identified in the product mixture by their mass spectra. For glycine, a shift in the molecular ion peak from 192 to 193 signals the isotopic labeling; for alanine a shift in the 206 ion peak to 207 confirms its presence. The characteristic fragmentation pattern given by the hydantoin confirms the identity of the derivative. Retention times for the labeled compounds agreed closely with those of standard derivatives as well.

The derivatized products of the isotope experiments were also analyzed by HPLC. The output indicated the presence of glycine, alanine, and small amounts of serine and aspartic acid (Table I, entry 11). The low concentration of serine prevented its detection by GC/mass spectroscopy. Silation of the PTH derivatives, followed by GC/MS analysis, failed to confirm the presence of aspartic acid in mixture. This is presumably because of the small concentration of the amino acid produced, and the large background signals of the silated sample.

The methylamine intermediate identified in the product mixture also contained the nitrogen-15 isotope. The reconstructed ion current (RIC) chromatogram in the GC/mass spectroscopic analysis obtained for a methylamine standard and the product of the isotope photoreaction is shown in Figure 2. The respective mass spectra are given in Figure 3. The presence of the isotope is clearly indicated by the shift in all major ion peaks to one higher mass unit.

Hydrogen Peroxide Decomposition Experiment. The presence of alcohol intermediates in the product mixtures, previous photocatalytic results on hydrocarbon decomposition reactions, and spin trapping experiments[5] suggest that hydroxyl radical (OH·) photogenerated at the semiconductor powder surface plays a major role in the synthesis reaction. Thus, the production of hydroxyl radical from a chemical source under similar experimental conditions should also produce amino acids. As a source of OH· we chose the decomposition of hydrogen peroxide at Pt foil.[11] This system has the advantage of being simple and adding a minimum of extraneous reactants to the CH_4–NH_3–H_2O mixture. The results of these experiments, presented in Table II show that amino acids are produced. The reaction was also carried out with methanol, an identified intermediate, as the carbon source. This procedure also produced amino acids. With CO_2 rather than CH_4 as a carbon source, no amino acid production was found. This experiment also serves as a control against accidental contamination of the reaction mixtures. Since the peroxide experiments produced the same amino acids as the photosynthetic experiment and the concentration ranges are similar, the results suggest that the synthetic reaction is initiated by hydroxyl radicals. The importance of hydroxyl radical in many chemical and biological systems has been previously documented.[12]

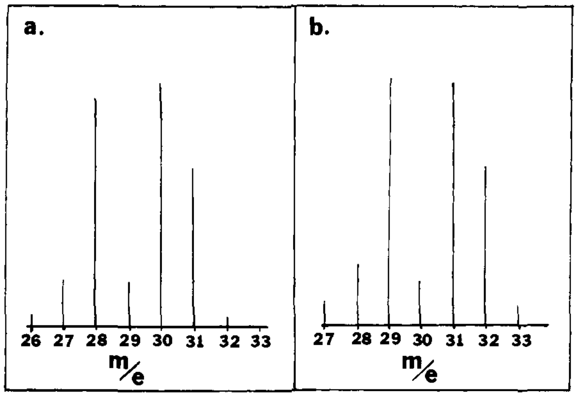

Figure 3. Mass spectra obtained for (a) methylamine standard in NH_3 and (b) Nitrogen-15 labeled methylamine from photoreaction. (See Experimental Section for details.)

Table II. Results of Peroxide Experiments[a]

system[a]	time, h	yield, nmol	relative amounts Asp	Ser	Glu	Gly	Ala
CH_4, NH_3, H_2O	240	72	1.6	0.7	0.18	1.0	1.2
CH_3OH, NH_3, H_2O	200	63	0.12	0.45	<0.01	1.0	0.5
CO_2, NH_3, H_2O	96	0					

[a] H_2O_2 decomposed at bright Pt; see Experimental Section for details.

Discussion

Reaction Mechanism. The experimental results clearly demonstrate the photoproduction of amino acids from the methane–NH_3–H_2O solutions. The presence of alcohol and amine intermediates, the fact that these may be employed as alternative starting materials, and the evidence of the intermediacy of OH· based on past photocatalytic experiments with TiO_2, as well as the reported H_2O_2 decomposition experiments, permit us to suggest a general mechanism for the reaction.

When light of energy greater than the anatase TiO_2 band gap (<405 nm) is absorbed, an electron/hole pair (e^-/h^+) is produced. Recombination is prevented by the rapid oxidation of H_2O or OH^- on the surface of the particle:

$$h^+ + H_2O \rightarrow OH\cdot + H^+ \qquad (1)$$

as well as the reaction of the electron at a Pt site. The role of the Pt, as previously suggested, is to catalyze the reduction re-

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(11) Hickling, A.; Wilson, W. H. *J. Electrochem. Soc.* **1951**, *98*, 425.

(12) (a) Dixon, W. T.; Norman, R. O. C. *Nature* (*London*) **1962**, *196*, 891. (b) *J. Chem. Soc., Perkin Trans. 2* **1975**, 308. (c) Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.

Table III. CO_2 Evolution Rates from Amino Acid Oxidation at Pt/TiO_2[a]

amino acid	irradiation time, h	rate of CO_2[b] evolution, μmol/h
glycine	24	44
alanine	41	18
aspartic acid	24	34

[a] 250 mg of Pt/TiO_2 in 30 mL of 0.1 M amino acid, irradiation intensity 34 mW/cm^2 and under O_2 free conditions. [b] Determined as $BaCO_3$, see Experimental Section.

action. A photogenerated electron is sufficiently energetic to reduce a proton at the platinized surface:

$$H^+ + e^- + Pt \rightarrow H\cdot\ (Pt) \qquad (2)$$

or the electron may be trapped on the TiO_2 surface as a Ti(III) state.[13]

The attack of a number of substrates by OH· is well-known. We suggest several possible reaction steps which can lead to production of the observed intermediates in the photoreaction under discussion. Methanol, ethanol, and methylamine have been detected as intermediates in the process. Hydrazine, the dimer product of $NH_2\cdot$ coupling, has not been detected in product mixtures, probably because it is readily decomposed. Amino acids could then be produced in successive free-radical reactions involving OH·, $NH_2\cdot$, and $CH_3\cdot$ and the intermediate species. Methanol, formaldehyde, and methane have been obtained in previously reported photoreductions of CO_2 at TiO_2 catalysts.[14]

$$CH_4 + \cdot OH \rightarrow CH_3\cdot + H_2O \qquad (3)$$

$$CH_4 + \cdot OH \rightarrow CH_3OH + H\cdot \qquad (4)$$

$$NH_3 + \cdot OH \rightarrow NH_2\cdot + H_2O \qquad (5)$$

$$NH_2\cdot + CH_3\cdot \rightarrow CH_3NH_2 \qquad (6)$$

$$2CH_3\cdot \rightarrow CH_3CH_3 \xrightarrow{\cdot OH} CH_3CH_2OH + H\cdot \qquad (7)$$

The free radicals can also attack the product amino acids. Decomposition of a number of carboxylic acids at Pt/TiO_2 has previously been demonstrated[4b] and a similar process occurs with the amino acids. In order to demonstrate this effect, the action of light on solutions of glycine, alanine, and aspartic acid containing Pt/TiO_2 suspensions was investigated. The results in Table III indicate that decarboxylation occurs, probably via the reaction

$$RC(NH_2)HCOOH \rightarrow RCH_2NH_2 + CO_2 \qquad (8)$$

Only trace amounts of alanine were detected in the aspartic acid photooxidaton experiment, so that both CO_2 groups are lost, with the intermediates probably adsorbed on the particle surface. Similar results have been reported for the reaction of adipic acid at Pt/TiO_2, where butane is the major product with only small amounts of valeric acid intermediate detected.[15] This photodecomposition of the amino acids prevents the buildup of appreciable quantities of these during the irradiation. Larger amounts could probably be produced in a recirculating or "Soxhlet extractor" type of arrangement where the product amino acids are removed continuously from contact with the Pt/TiO_2 particles. The fact that products and intermediates are undergoing photodecomposition reactions prevents an estimate of the actual quantum yields. The overall yields are clearly very small since the radiation absorbed by the TiO_2 powder in these experiments is $\sim 10^{18}$ photons/s and the yields ~nmol/day.

Implications in Chemical Evolution. In a previous communication[1] we suggested that processes such as those described here may occur in nature and may have played a role in the terrestrial production of amino acids from components of the primordial atmosphere. However, unplatinized materials, Fe_2O_3, and ilmenite have not shown the production of amino acids at detectable levels. We might note that Oliver and co-workers[16] in a study of the effect of suspended sediments on the photolysis of organics in waters found that while anatase caused appreciable reaction, TiO_2-bearing clays (e.g., montmorillonite, kaolinite) did not. However, Schrauzer et al.[17] have reported photoreduction of N_2 on Ti-bearing desert sands. Natural ores or minerals for the amino acid photosynthesis reaction would require both the OH· generation ability and stability of TiO_2 and efficient reduction sites for removal of the photogenerated electrons.

A second aspect of the problem of chemical evolution pertains to the nature of the primordial atmosphere. Recently the view has been expressed[17] that rather than the reducing atmosphere (containing CH_4 and NH_3) that has previously been assumed, the early atmosphere was more oxidizing (e.g., containing CO_2 and N_2). While we have not yet attempted amino acid photosynthesis with these components, we might note that reduction of CO_2 to formaldehyde, methanol, and methane[14] and reduction of N_2 to NH_3[17] in low yields have been reported on irradiated TiO_2 (and other semiconductors). Thus, a route to amino acids from the more oxidizing atmosphere appears possible.

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