Heterogeneous photosynthetic production of amino acids from methane-ammonia-water at platinum/titanium dioxide. Implications in chemical evolution

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benzocyclobutene dimerization method is that it is highly efficient and relatively short so that adequate quantities of superphene are readily available for such studies.

With the syntheses of [2.2.2.2](1,2,3,4)-, [2.2.2.2.2](1,2,3,4,5)-, and [2.2.2.2.2.2](1,2,3,4,5,6)cyclophanes described in these two communications, all of the possible isomers of the [2*] series of cyclophanes are now known. However, as for multibridged cyclophanes containing polycyclic and heterocyclic moieties, this potential is being explored.

Acknowledgment. We thank the National Science Foundation for their support of this investigation.

References and Notes

(2) We are indebted to Professor H. Hopf for suggesting this trivial name to us.
(7) Satisfactory spectral data, elemental analyses, and/or high-resolution mass spectra are available for all new compounds being reported. NMR spectra were measured in deuterochloroform solutions with tetramethylsilane as an internal standard; and mass spectra were measured at 70 eV.
(10) When 7 was carried through the same sequence, pyrolysis of the corresponding dichloro derivative gave only polymer.
(11) Shortly after completing the synthesis of 8, we learned from Professor H. Hopf, University of Würzburg, that his research group has successfully prepared the parent molecule: [2.2.2.2](1,2,3,4)cyclophane.
(12) This is accompanied by the corresponding monoaquide (25% yield), mp 162–183°C.
(13) The preparation of the remaining member, [2.2.2](1,2,3,4)cyclophane, is described in the Undergraduate Thesis of B. Neuschwander, University of Oregon, 1978.
(14) See, for example, the preparation of [2.2.2](1,2,3,4)cyclophane (G. D. Ewing and V. Boekelheide, J. Chem. Soc., Chem. Commun., in press).

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Heterogeneous Photosynthetic Production of Amino Acids from Methane-Ammonia-Water at Pt/TiO2: Implications in Chemical Evolution

Sir:

Previous studies from this laboratory have demonstrated that irradiation of platinized n-type TiO2 suspensions with a xenon lamp or sunlight can promote several solution reactions, such as the photo-Kolbe reaction, in which acetic acid is decomposed to methane and CO2.1 Recent experiments employing spin trapping methods and electron spin resonance detection during illumination of aqueous solutions containing such suspensions3 have demonstrated the intermediacy of hydroxyl radicals under these conditions.1 The presence of such a reactive intermediate suggested the possibility of synthesis of amino acids by irradiation of methane-ammonia-water mixtures in the presence of semiconductor powder suspensions; electrical discharges through similar gaseous mixtures are known to produce amino acids.5,6

Irradiation of 20 mL of aqueous 2 M NH4Cl or NH3 (~28%) solutions, deaerated first with nitrogen or argon, under slow continuous bubbling of methane in the presence of 100 mg of Pt/TiO2 with a 2.5-kW xenon lamp operated at 1.6 kW for 64–66 h produced a mixture of amino acids. The total yield of amino acids was ~0.5 μmol for the NH4Cl and ~0.2 μmol for the aqueous NH3, with the mixture consisting of glycine, alanine, serine, aspartic acid, and glutamic acid. Analysis was carried out with a Beckman Model 120C amino acid analyzer and the identity and amount of acid was estimated by comparison with a standard mixture.8 An additional, as yet unidentified, peak was found in the irradiated mixture sample which was not present in the standard. Several control experiments were also carried out to eliminate the possibility of sample contamination or other paths as the source of the amino acids (Table I).

The results demonstrate the heterogeneous photosynthesis of amino acids under irradiation with visible and near-UV light. The action spectrum for this reaction probably corresponds to that found for the photo-Kolbe reaction with Pt/TiO2 with a threshold at 420 nm.9 The mechanism of the process, which is currently under investigation, begins with production of holes and electrons upon light absorption by the TiO2. Oxidation leading to the amino acids then could proceed upon production of OH radicals, and probably other intermediates (e.g., -NH2). Reaction of OH radicals with methane leading to CH3 radicals is well documented.10 Reduction occurs at the Pt sites, leading to H atoms and, ultimately, under these reducing conditions, to H2. The absence of reaction with unplatinized TiO2 can be ascribed to inefficient reductive sites for hydrogen production in this case, as has been previously found for other photocatalytic processes.1 Photocatalytic oxidation at TiO2 alone could probably take place in the presence of easily reducible substances, such as oxygen or ferric iron. The overall reaction as described here at Pt/TiO2, however, is photosynthetic, involving a net storage of light energy. For example for the overall reaction

\[
2\text{CH}_4 + \text{NH}_3 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{NCH}_2\text{COOH} + 5\text{H}_2
\]

\[\Delta G^\circ = 55.4 \text{kcal/mol} \]11

The results reported here may also be relevant to the initial stages of chemical evolution and the prebiological synthesis of organic compounds from components of the reducing Precambrian atmosphere.12,13 While previous experiments have shown similar synthesis using rather energetic sources, e.g., electric discharges or UV light,1.4 these results demonstrate this synthesis in solution with radiation characteristic of the terrestrial solar spectrum.14 The continuous production of such species by inorganic systems such as TiO2 under solar irradiation could have been a source of nutrients for the initially evolved heterotrophic organisms and served as an abiotic form of photosynthesis until biological photosynthetic systems based on chlorophyll evolved; other aspects of the chemical evolution of photosynthesis have been discussed recently.16 Heterogeneous photoprocesses such as those described could also have contributed to the nonbiological production of early Precambrian oxygen; arguments against total biological sources for atmospheric oxygen have appeared.17 While Pt/TiO2 itself

| Table I. Effect of Solution, Light, and Catalyst on Photosynthesis of Amino Acids |
|---|---|---|---|
| solution composition | catalyst | illumination | amino acid yield, μmol |
| NH3 | H2O | CH4 | Pt/TiO2 | Xe lamp, 66 h | ~0.2 |
| 2 M NH4Cl | CH4 | Pt/TiO2 | Xe lamp, 64 h | ~0.5 |
| 2 M NH4Cl, CH4 | Pt/TiO2 | Control Experiments | none, 66 h | none |
| 2 M NH4Cl, CH4 | Pt/TiO2 | Xe lamp, 66 h | none |
| 2 M NH4Cl, CH4 | TiO2(a.u) | Xe lamp, 66 h | none |
| 2 M NH4Cl | none | none | none |

(1) 20 mL of deaerated solution under continuous addition of CH4. (2) 100 mg of Pt/TiO2 or unreduced anatase(a.u). (3) 2.5-kW xenon lamp operated at 1.6 kW. (4) Less than 1 nmol.
represents an unlikely substance for such terrestrial photosynthetic processes, there are a number of other inorganic semiconductor systems, such as Fe₂O₃ and WO₃, which may be capable of similar reactions. Such processes are currently under investigation in this laboratory.³

References and Notes

(1) (a) Kraeutler, B.; Bard, A. J. Am. Chem. Soc. 1978, 100, 2239; (b) ibid., 5985.


(7) Produced by irradiation of a suspension of reduced nitrate in solution containing PtCl₄⁻ in a 1:1 mixture of water and acetic acid at pH 3—5.

(8) The standard contained 33 mmol each of the protein amino acids. The relative amounts of amino acids produced in the irradiation experiments follow: Nle Glu (0.4); Ser (0.3) Ala (0.2); Asp (0.2); Nle Glu solution. Glu (1) Glu (1) Ser (0.5) Ala (0.6) Asp (0.7). This identification assumes that amino acids produced by irradiation are those in the protein amino acid standard. Attempts at mass spectral identification of the reaction products are in progress.


(14) Recent experiments have shown that amino acid production with irradiation of a suspension of reduced anatase powder in a 1:1 mixture of water and acetic acid at pH 3—5.

(15) Dunn W.; Bard, A. J., unpublished work.


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Three-Center Oxidative Addition.
Formation, Structure, and Dissociation of (PhC₂H₄NC)₂RhI₂⁺ and Related Cations

Sir:

Although a wide variety of oxidative addition reactions involving low-valent metal complexes have been reported, only a few metal complexes are known to undergo simultaneous two-center oxidative addition. Most of these involve additions to complexes in which the two metal centers are held in fixed, close proximity by bridging ligands. An exception exists in the case of ion one and bromine addition to (RNC)₂Rh⁺ where, in addition to normal oxidative addition to form (RNC)₂RhX₂⁺, two-center addition also occurs to form X(RNC)₂RhRhX₂(RNC)₂X₂⁺.⁴⁻⁵ We now report the first case of three-center oxidative addition; this also involves the rhodium isocyanide family of compounds.

Addition of 1 mol of iodine to 3 mol of [C₆H₆C₆H₄NC]₂RhI₂Br (X = 1 or Br) in dichloromethane produces a violet solution from which [(C₆H₆C₆H₄NC)₂RhI₂Br]X₃ is readily crystallized in 85% yield by the addition of cyclohexane. The infrared spectra (PCN 2327 cm⁻¹ (X = Br); PCN 2235, 2209 cm⁻¹ (X = Nujol mulls) of these salts indicate that only terminal isocyanide ligands are present. Similar compounds, e.g., [(n-C₄H₉NC)₂RhI₂]I (PCN 2227, 2205 cm⁻¹), have been obtained by air oxidation of methanol solutions of (RNC)₄Rh⁺ in the presence of excess iodide followed by recrystallization from dichloromethane-cyclohexane.

The structure of one typical salt, [(C₆H₆C₆H₄NC)₂RhI₂Br]I (1) has been determined by X-ray crystallography. Compound 1 crystallizes as violet plates from dichloromethane-cyclohexane in space group P1 with cell dimensions a = 11.78 Å, b = 12.75 Å, c = 16.09 Å. α = 81.74°, β = 81.19°, γ = 85.85°. V = 2364 Å³. ρexp = 2.98 g cm⁻³. A crystal of dimensions 0.50 × 0.35 × 0.425 mm was selected for data collection. A total of 6169 unique reflections were collected at 140 K using a Syntex P2, automatic diffractometer graphite-monochromatized Mo Kα radiation and a variable-speed ω scan technique. The solution and refinement of data were carried out using Patterson, Fourier, and full-matrix least-squares methods. Refinement using intensity data having F₂ > 3σ(F²) (4586 reflections) and anisotropic thermal parameters for I, Rh, and Br lead to a conventional R index of 0.073.

The crystal contains the complex cation, which possesses a center of symmetry and is shown in Figure 1, and individual bromide ions. The coordination about each rhodium is pyramidal with four isocyanide ligands at the corners of a square; these squares are staggered 38° from one rhodium to the next. The I—Rh—Rh—I unit is nearly linear. The Rh—Rh and Rh—I bond lengths are similar those of the related cation, [(RNC)₄Rh⁺].