

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

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J. Am. Chem. Soc., **1979**, 101 (11), 3127-3128 • DOI: 10.1021/ja00505a054 • Publication Date (Web): 01 May 2002

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

With the syntheses of [2.2.2.2](1,2,3,4)-, [2.2.2.2.2.2](1,2,3,4,5)-, and [2.2.2.2.2.2.2.2](1,2,3,4,5,6)cyclophanes described in these two communications, all of the possible isomers of the [2ⁿ] series of cyclophanes are now known.¹³ However, the benzocyclobutene dimerization method should have broad application for the syntheses of known cyclophanes,¹⁴ as well 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

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- (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 monoaldehyde (25% yield), mp 182–183 °C.
- (13) The preparation of the remaining member, [2.2.2](1,2,3)cyclophane, is described in the Undergraduate Thesis of B. Neuschwander, University of Oregon, 1978.
- (14) See, for example, the preparation of [2.2.2](1,2,4)cyclophane (G. D. Ewing and V. Boekelheide, *J. Chem. Soc., Chem. Commun.*, in press).

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Received February 6, 1979

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.^{1,2} 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.⁴ 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/TiO₂⁷ 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

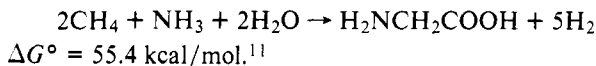
Table I. Effect of Solution, Light, and Catalyst on Photosynthesis of Amino Acids

solution composition ^a	catalyst ^b	illumination ^c	amino acids yield, μmol
NH ₃ , H ₂ O, CH ₄	Pt/TiO ₂	Xe lamp, 66 h	~0.2
2 M NH ₄ Cl, CH ₄	Pt/TiO ₂	Xe lamp, 64 h	~0.5
Control Experiments			
2 M NH ₄ Cl, CH ₄	Pt/TiO ₂	none, 66 h	none ^d
2 M NH ₄ Cl, CH ₄	none	Xe lamp, 66 h	none ^d
2 M NH ₄ Cl, CH ₄	TiO ₂ (a.u)	Xe lamp, 66 h	none ^d
2 M NH ₄ Cl	none	none	none ^d

^a 20 mL of deaerated solution under continuous addition of CH₄.
^b 100 mg of Pt/TiO₂⁷ or unreduced anatase(a.u). ^c 2.5-kW xenon lamp operated at 1.6 kW. ^d Less than 1 nmol.

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 atoms⁴ 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



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,^{5,6} 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

represents an unlikely substance for such terrestrial photosynthetic processes, there are a number of other inorganic semiconductor systems, such as Fe_2O_3 and WO_3 ,² which may be capable of similar reactions. Such processes are currently under investigation in this laboratory.¹⁸

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Received January 8, 1979

Three-Center Oxidative Addition.

Formation, Structure, and Dissociation of $(\text{PhCH}_2\text{NC})_{12}\text{Rh}_3\text{I}_2^{3+}$ 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 iodine and bromine addition to $(\text{RNC})_4\text{Rh}^+$ where, in addition to normal oxidative addition to form $(\text{RNC})_4\text{RhX}_2^+$,² two-center addition also occurs to form $\text{X}(\text{RNC})_4\text{RhRh}(\text{CNR})_4\text{X}^{2+}$.^{3,4} 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 $[(\text{C}_6\text{H}_5\text{CH}_2\text{NC})_4\text{Rh}]^+\text{X}^-$ ($\text{X} = \text{I}$ or Br) in dichloromethane produces a violet solution from which $[(\text{C}_6\text{H}_5\text{CH}_2\text{NC})_{12}\text{Rh}_3\text{I}_2]\text{X}_3$ is readily crystallized in 85% yield by the addition of cyclohexane. The infrared spectra (ν_{CN} 2236 (sh), 2213 cm^{-1} ($\text{X} = \text{Br}$); ν_{CN} 2235, 2209 ($\text{X} = \text{I}$) as Nujol mulls) of these salts indicate that only terminal isocyanide ligands are present. Similar compounds, e.g., $[(n\text{-C}_4\text{H}_9\text{NC})_{12}\text{Rh}_3\text{I}_2]\text{I}_3$ (ν_{CN} 2227, 2205 cm^{-1}), have been obtained by air oxidation of methanol solutions of

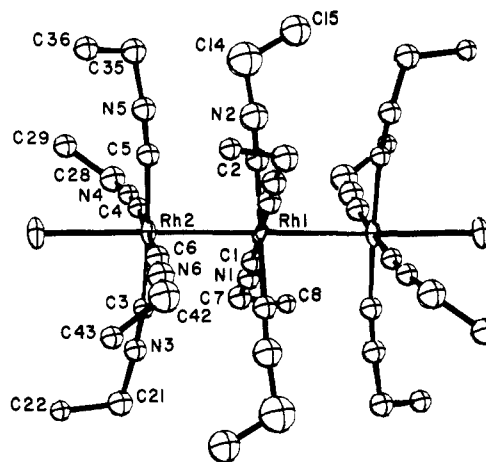


Figure 1. An ORTEP drawing of $[(\text{C}_6\text{H}_5\text{CH}_2\text{NC})_{12}\text{Rh}_3\text{I}_2]^{3+}$ showing 50% thermal ellipsoids. Bond lengths follow: Rh-Rh, 2.796 (1), Rh-I, 2.761 (1) Å. The Rh-Rh-I angle is 175.5 (1)°. To avoid cluttering of the drawing, only the first carbon atom of each phenyl group has been shown.

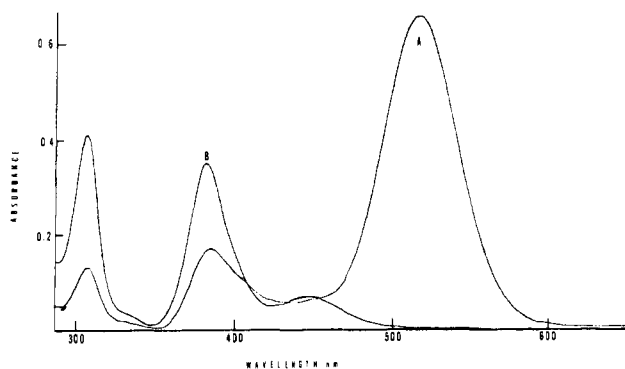


Figure 2. The electronic spectrum of a solution initially containing 7.6×10^{-5} M $[(n\text{-C}_4\text{H}_9\text{NC})_{12}\text{Rh}_3\text{I}_2]^{3+}$ in acetonitrile with a 1-mm path length cell: curve A, sample within 5 min of preparation; curve B, after 2 h. The absorption at 525 nm is uniquely associated with $[(n\text{-C}_4\text{H}_9\text{NC})_{12}\text{Rh}_3\text{I}_2]^{3+}$. Absorption bands of pure $(n\text{-C}_4\text{H}_9\text{NC})_4\text{Rh}^+$ occur at 381 nm (ϵ 11 000) and 309 (36 600), while $(n\text{-C}_4\text{H}_9\text{NC})_8\text{Rh}_2\text{I}_2^+$ has absorption maxima at 448 and 380 nm and $(n\text{-C}_4\text{H}_9\text{NC})_4\text{RhI}_2^+$ has a maximum at 387 nm (ϵ 11 200).

$[(\text{RNC})_4\text{Rh}]^+\text{I}^-$ in the presence of excess iodide followed by recrystallization from dichloromethane-cyclohexane.

The structure of one typical salt, $[(\text{C}_6\text{H}_5\text{CH}_2\text{NC})_{12}\text{Rh}_3\text{I}_2]\text{Br}_3$ (**1**) has been determined by X-ray crystallography. Compound **1** crystallizes as violet plates from dichloromethane-cyclohexane in space group $P\bar{1}$ with cell dimensions $a = 11.788$ (7), $b = 12.750$ (6), $c = 16.095$ (6) Å; $\alpha = 81.74$ (3), $\beta = 81.19$ (4), $\gamma = 85.85$ (4)°; $V = 2364$ Å³; ρ_{exptl} (298 K) = 1.54 g cm⁻³; $Z = 1$; μ_{Mo} = 25.4 cm⁻¹. A crystal of dimensions 0.050 × 0.35 × 0.425 mm was selected for data collection. A total of 6169 unique reflections were collected at 140 K using a Syntex P2₁ automatic diffractometer graphite-monochromatized Mo K α 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 $F_o^2 > 3\sigma(F_o^2)$ (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 pseudooctahedral 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-Rh-I unit is nearly linear. The Rh-Rh and Rh-I bond lengths are similar to those of the related cation,