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]-(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 $[2^n]$ 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.

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References and Notes

(1) F. Vögtle and P. Neumann, *Angew. Chem.*, **84**, 75 (1972); *Angew. Chem., Int. Ed. Engl.*, 11, 73 (1972).

(2) We are indebted to Professor H. Hopf for suggesting this trivial name to us.

(3) P. F. T. Schirch and V. Boekelheide, *J. Am. Chem. Soc.*, preceding paper in this issue.

(4) V. Boekelheide and G. Ewing, *Tetrahedron Lett.*, 4245 (1978).

(5) L. I. Smith and C. W. MacMullen, *J. Am. Chem. Soc.*, **58**, 629 (1936).

(6) R. Gray, L. G. Harruff, J. Krymowski, J. Peterson, and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2892 (1978). Cf. P. Schiess, M. Heitzmann, S. Rutschmann, and R. Stäheli, *Tetrahedron Lett.*, 4569 (1978).

(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 deuteriochloroform solutions with tetramethylsilane as an internal standard; and mass spectra were measured at 70 eV.

(8) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4267 (1959).

(9) A. Rieche, H. Gross, and E. Höft, *Chem. Ber.*, **93**, 88 (1960).

(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 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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Heterogeneous Photosynthetic Production of Amino Acids from Methane–Ammonia–Water at Pt/TiO_2. Implications in Chemical Evolution

Sir:

Previous studies from this laboratory have demonstrated that irradiation of platinized n-type TiO_2 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 CO_2.[1,2] Recent experiments employing spin trapping methods and electron spin resonance detection during illumination of aqueous solutions containing such suspensions[3] 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 NH_4Cl or NH_3 ($\sim$28%) solutions, deaerated first with nitrogen or argon, under slow continuous bubbling of methane in the presence of 100 mg of Pt/TiO_2[7] 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 $\sim$0.5 μmol for the NH_4Cl and $\sim$0.2 μmol for the aqueous NH_3, 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).

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_2O, CH_4	Pt/TiO_2	Xe lamp, 66 h	$\sim$0.2
2 M NH_4Cl, CH_4	Pt/TiO_2	Xe lamp, 64 h	$\sim$0.5
	Control Experiments		
2 M NH_4Cl, CH_4	Pt/TiO_2	none, 66 h	none[d]
2 M NH_4Cl, CH_4	none	Xe lamp, 66 h	none[d]
2 M NH_4Cl, CH_4	TiO_2(a,u)	Xe lamp, 66 h	none[d]
2 M NH_4Cl	none	none	none[d]

[a] 20 mL of deaerated solution under continuous addition of CH_4. [b] 100 mg of Pt/TiO_2[7] or unreduced anatase(a,u). [c] 2.5-kW xenon lamp operated at 1.6 kW. [d] Less than 1 nmol.

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/TiO_2, 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 TiO_2. Oxidation leading to the amino acids then could proceed upon production of OH radicals, and probably other intermediates (e.g., $\cdot NH_2$). Reaction of OH radicals with methane leading to CH_3 radicals is well documented.[10] Reduction occurs at the Pt sites, leading to H atoms[4] and, ultimately, under these reducing conditions, to H_2. The absence of reaction with unplatinized TiO_2 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 TiO_2 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/TiO_2, however, is photosynthetic, involving a net storage of light energy. For example for the overall reaction

$$2CH_4 + NH_3 + 2H_2O \rightarrow H_2NCH_2COOH + 5H_2$$

$\Delta G° = 55.4$ 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,[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 TiO_2 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/TiO_2 itself

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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]

References and Notes

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

(2) (a) Frank, S. N.; Bard, A. J. *J. Am. Chem. Soc.* **1977**, *99,* 303; (b) *J. Phys. Chem.* **1977**, *81,* 1484.

(3) Kraeutler, B.; Jaeger, C. D.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100,* 4903.

(4) Jaeger, D. C.; Bard, A. J., manuscript in preparation.

(5) (a) Miller, S. L. *Science* **1953**, *117,* 528; (b) *J. Am. Chem. Soc.* **1955**, *77,* 2351.

(6) Miller, S. L.; Urey, H. C. *Science* **1959**, *130,* 245.

(7) Produced by irradiation of a suspension of reduced anatase powder in a solution containing $PtCl_6{}^{2-}$ in a 1:1 mixture of water and acetic acid at pH ~5: Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100,* 4317.

(8) The standard contained 33 nmol each of the protein amino acids. The relative amounts of amino acids produced in the irradiation experiments follow: NH_3 solution, Gly (1):Glu (0.4):Ser (0.3):Ala (0.2):Asp (0.2); NH_4Cl solution, Gly (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.

(9) Gray, R. C.; Bard, A. J. *Anal. Chem.* **1978**, *50,* 1262.

(10) Anbar, M.; Meyerstein, D.; Neta, P. *J. Chem. Soc. B* **1966**, 742 and references therein.

(11) Weast, R. C., Ed. "Handbook of Chemistry and Physics", 56th Ed.; CRC Press: Cleveland, 1975.

(12) Dickerson, R. E. *Sci. Am.* **1978**, *239,* 70.

(13) Fox, S. W.; Dose, K. "Molecular Evolution and the Origin of Life", Marcel Dekker: New York, 1977.

(14) Recent experiments[15] have shown that amino acid production with irradiation by sunlight is also possible. Thus irradiation of 2 L of a 2 M NH_4Cl solution contained in a Pyrex flask with TiO_2/Pt for 13 days yielded micromole amounts of glycine and alanine, with trace amounts of aspartic acid.

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

(16) Krasnovsky, A. A. *Origins Life* **1976**, *7,* 133.

(17) Towe, K. M. *Nature (London)* **1978**, *274,* 657.

(18) The support of this research by the National Science Foundation and Robert A. Welch Foundation and by a grant to H.R. by Heinrich Hertz-Stiftung, Düsseldorf, is gratefully acknowledged.

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Three-Center Oxidative Addition. Formation, Structure, and Dissociation of $(PhCH_2NC)_{12}Rh_3I_2{}^{3+}$ 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 $(RNC)_4Rh^+$ where, in addition to normal oxidative addition to form $(RNC)_4RhX_2{}^+$,[2] two-center addition also occurs to form $X(RNC)_4RhRh(CNR)_4X^{2+}$.[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 $[C_6H_5CH_2NC)_4Rh]X$ (X = I or Br) in dichloromethane produces a violet solution from which $[(C_6H_5CH_2NC)_{12}Rh_3I_2]X_3$ is readily crystallized in 85% yield by the addition of cyclohexane. The infrared spectra (ν_{CN} 2236 (sh), 2213 cm^{-1} (X = Br); ν_{CN} 2235, 2209 (X = I) as Nujol mulls) of these salts indicate that only terminal isocyanide ligands are present. Similar compounds, e.g., $[(n\text{-}C_4H_9NC)_{12}Rh_3I_2]I_3$ (ν_{CN} 2227, 2205 cm^{-1}), have been obtained by air oxidation of methanol solutions of $[(RNC)_4Rh]I$ in the presence of excess iodide followed by recrystallization from dichloromethane–cyclohexane.

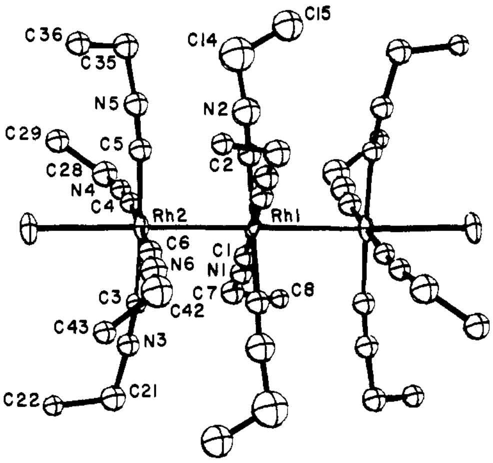

Figure 1. An ORTEP drawing of $[(C_6H_5CH_2NC)_{12}Rh_3I_2]^{3+}$ showing 50% thermal ellipsoids. Bond lengths follow: Rh–Rh, 2.796 (1), Rh–I, 2.761 (1) Å. The Rh–Rh–I angle is 175.5 (1)°. To avoid cluttering of the drawing, only the first carbon atom of each phenyl group has been shown.

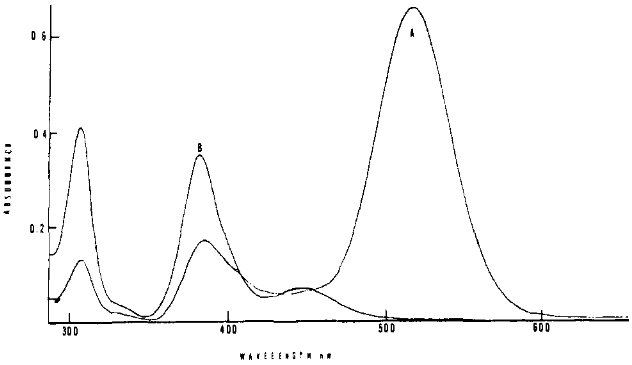

Figure 2. The electronic spectrum of a solution initially containing 7.6 × 10^{-5} M $[(n\text{-}C_4H_9NC)_{12}Rh_3I_2]I_3$ in acetonitrile with a 1-mm path length cell: curve A, sample within 5 min of preparation; curve B, after 2 h. The absorption at 525 nm is uniquely associated with $[(n\text{-}C_4H_9NC)_{12}Rh_3I_2]^{3+}$. Absorption bands of of pure $(n\text{-}C_4H_9NC)_4Rh^+$ occur at 381 nm (ϵ 11 000) and 309 (36 600), while $(n\text{-}C_4H_9NC)_8Rh_2I_2{}^+$ has absorption maxima at 448 and 380 nm and $(n\text{-}C_4H_9NC)_4RhI_2{}^+$ has a maximum at 387 nm (ϵ 11 200).

The structure of one typical salt, $[(C_6H_5CH_2NC)_{12}Rh_3I_2]Br_3$ (**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; α = 81.74 (3), β = 81.19 (4), γ = 85.85 (4)°; V = 2364 Å^3; 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 $P2_1$ 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 $F_o{}^2 > 3\sigma(F_o{}^2)$ (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 those of the related cation,

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