than $W_5P_2O_{23}^{6-}$. Similarly, the replacement of sodium tungstate and sodium dihydrogen phosphate by potassium tungstate and potassium dihydrogen phosphate in the reaction with cesium chloride to form $Cs_7Na_2W_{10}PO_{37}$ does not give $Cs_7K_2W_{10}PO_{37}$; salts of $W_9PO_{34}^{9-}$ are obtained instead. Some effects of counterions on the chemistry of $Cs_6W_5P_2O_{23}$ are shown in Scheme I. The importance of counterions in determining solid-state structure raises the question of whether these new tungstophosphate structures persist in solution. The fact that all of the new salts can be successfully recrystallized from water cannot be regarded as conclusive evidence. Solutions of these salts each exhibit a single ^{31}P resonance ($Cs_6W_5P_2O_{23}$, −2.4 ppm; $Cs_7W_{10}PO_{36}$, −10.5 ppm; $Cs_7Na_2W_{10}PO_{37}$, 1.2 ppm) which suggests at least that they each form only one species in solution. We can speculate that the structures persist in solution for a finite time, perhaps stabilized by ion pairing. We hope to obtain more meaningful information on this point from future ^{183}W NMR studies.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters and structure amplitudes (63 pages). Ordering information is given on any current masthead page.

---

(8) **Crystal structure information**: Monoclinic, space group $P2_1/c$; at −100 °C, a = 13.009 (2), b = 15.974 (3), c = 17.087 (3) Å; β = 98.93 (1)°; V = 3508 Å^3; Z = 4. Syntex P3 diffractometer, graphite monochromator, Mo Kα radiation, λ = 0.71069 Å, ω scans of 1.0°, $4 < 2\theta < 50°$, 6172 reflections. An empirical absorption correction based on ψ-scan data was applied; the "transmission factors" ranged from 0.475 to 0.996. The structure was refined by full-matrix, least-squares techniques: 5201 reflections with $I > 2\sigma(I)$, 240 variables (W and Cs with anisotropic thermal parameters, P and O with isotropic paramters, no hydrogen atoms included), R = 0.038, R_w = 0.037. The three water molecules labeled OW(7), OW(8), and OW(9) originally showed up in a difference Fourier with magnitudes which were half those of the other water oxygen atoms. It appears that the area is occupied half the time by two water molecules, OW(7) and OW(9), and half the time by just one, OW(8). The final difference map showed only residues of the W and Cs atoms, the largest of which had a magnitude of 1.2 e Å^{-3}. The mathematical and computational details may be found in ref 10.

(9) **Crystal structure information** (where different from ref 8): Orthorhombic, space group $P2_12_12$; at −100 °C, a = 12.401 (3), b = 18.948 (4), c = 9.636 (2) Å; V = 2264 Å^3; Z = 2 (the heteropolyanion sits on a crystallographic twofold axis). Reflections (2952) were measured in the range $4 < 2\theta < 55°$. "Transmission factors" ranged from 0.428 to 0.994. Refinement information: 2665 reflections with $I > 3\sigma(I)$, 166 variables, R = 0.047, R_w = 0.054 (the enantiomeric structure refined to R = 0.057). All of the major residual peaks in the final difference, 1.4–1.8 e Å^{-3}, were associated with the W atoms.

(10) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030–2032.

Photogeneration of an Active Formate-Decomposition Catalyst

A. D. King, Jr.,* R. B. King, and E. L. Sailers, III

Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Received September 15, 1980

Simple group 6 metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) have been shown to be active homogeneous catalysts for the water gas shift reaction under basic conditions.[1] These catalysts are of particular interest in view of their high sulfur tolerance.[2] Recent mechanistic studies[3,4] strongly suggest that these catalysts function through the decomposition of an intermediate formatopentacarbonylmetallate anion $HCO_2M(CO)_5^-$ (M = Cr, Mo, W) produced by formate ion addition to $M(CO)_5$ resulting from the reversible CO dissociation of corresponding $M(CO)_6$ species as summarized in the following equations:

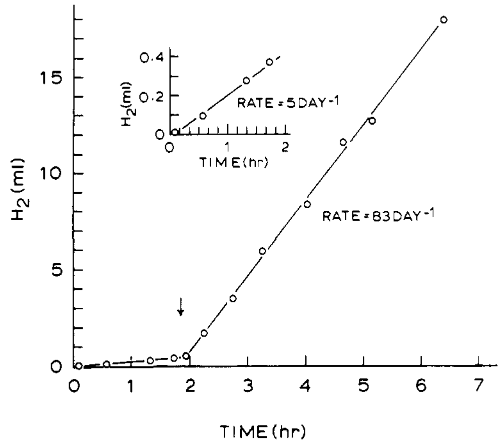

Figure 1. Hydrogen production (mL at 1 atm, 25 °C) from the catalytic decomposition of formate ion as a function of time. Catalyst solution: $W(CO)_6$ (0.039 mmol), $NaHCO_2$ (40 mmol), 200 mL (25:75 H_2O–2-ethoxyethanol); T = 75 °C. The arrow indicates the time at which the formerly dark solution is illuminated by sunlight.

$$CO + OH^- \rightarrow HCO_2^- \quad (1)$$

$$M(CO)_6 \rightleftharpoons M(CO)_5 + CO \quad (2)$$

$$M(CO)_5 + HCO_2^- \rightarrow HCO_2M(CO)_5^- \quad (3)$$

$$HCO_2M(CO)_5^- \rightarrow HM(CO)_5^- + CO_2 \quad (4)$$

$$HM(CO)_5^- + H_2O \rightarrow H_2M(CO)_5 + OH^- \quad (5)$$

$$H_2M(CO)_5 \rightarrow M(CO)_5 + H_2 \quad (6)$$

It is well-known that group 6 metal hexacarbonyls are readily photolyzed by visible light to produce the same $M(CO)_5$ species as shown resulting from the thermal dissociation of $M(CO)_6$ indicated in eq 2.[5] This suggests the photochemical dissociation of $M(CO)_6$ to produce $M(CO)_5$ can be substituted for the thermal dissociation step involved in the above sequence of reactions. This could provide facile entry into the main part of the catalytic cycle (eq 3–6), thereby leading to enhanced catalytic activity at relatively low temperatures. This communication describes preliminary observations on the decomposition of formate ion by eq 3–6 (M = W) using photolysis to generate the required $W(CO)_5$ intermediate.

Figure 1 shows hydrogen production as a function of time over 200 mL of a solution [25:75 water–2-ethoxyethanol (v/v)] containing sodium formate (0.20 M) and 0.039 mmol of $W(CO)_6$ maintained under an atmosphere of CO (P_{CO} = 1 atm) at 75 °C.[6] The nearly horizontal portion of the data represents hydrogen production from this solution made up and maintained under extremely low-light conditions. This colorless solution containing dissolved $W(CO)_6$ exhibits a very low level of thermal catalytic activity at 75 °C which is shown in the inset of Figure 1 to

---

(1) King, R. B.; Frazier, C. C.; Hanes, R. M.; King, A. D., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 2925.

(2) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Chem. Soc., Chem. Commun.* **1980**, 529.

(3) King, R. B.; King, A. D., Jr.; Yang, D. B. *ACS Symp. Ser.*, in press.

(4) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.*, in press.

(5) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

(6) The photocatalytic experiments described here were carried out in 250-mL Schlenk tubes fitted with an arrangement of glass tees such that one septum and four rubber bulbs were maintained in contact with the gas phase (100 mL) contained over the solution (200 mL) within the tube. This arrangement provided for expansion during gas production so that GLC analysis could be easily effected using Pressure-Loc syringes for gas sampling. Hydrogen analyses were performed by using a 8-ft column of 13X molecular sieve with argon as a carrier gas at 50 °C. CO_2 and CO analyses were carried out by using a Fisher Model 1200 gas partitioner fitted with the standard Columnpak PQ and 13X molecular sieve columns at 50 °C, using helium as the carrier gas. Prior determined external sensitivity factors were used to convert GLC peaks to gas sample volumes. Simultaneous heating and illumination was accomplished by using an electrical heating mantle connected to an Omega Model 49 proportioning controller with the thermocouple sensor held tightly against the external surface of the Schlenk flask below the liquid level with electrical tape. When insulated with glass wool, this arrangement provided adequate temperature control for these experiments (±1 °C).

0002-7863/81/1503-1867$01.25/0

correspond to a turnover number of only 5 day^{-1}. Illumination of this solution, maintained at 75 °C, with sunlight causes the solution to become yellow and leads to an abrupt increase in the rate of hydrogen production corresponding to a turnover number of 83 day^{-1}. The hydrogen production by the photolyzed solution is catalytic with respect to $W(CO)_6$, since the production of 18 mL of H_2 constitutes approximately 16 turnovers of catalyst on the basis of $W(CO)_6$ initially present in the solution. The rate of production of CO_2 is found to equal that for H_2 within experimental error for this system in accordance with eq 4–6.[7] Likewise the loss of CO over the duration of the experiment is exactly accounted for by sampling losses, thus indicating that reaction 1 does not proceed to a measurable extent under these conditions. The rate of production of H_2 following illumination is found to be substantially the same (76 day^{-1} measured over four turnovers) when this same experiment is repeated under a N_2 atmosphere.

No measurable hydrogen production is observed with either nonilluminated or photolyzed solutions of $W(CO)_6$ when sodium formate is absent or is replaced by potassium hydroxide. As noted earlier, the reaction of OH^- with CO to produce formate (eq 1) is very slow at 75 °C. Thus the negative results obtained with potassium hydroxide serve to eliminate from consideration any catalytic sequence involving direct base attack on $W(CO)_6$ under the conditions of these experiments. Such a mechanism has been invoked for the water gas shift reaction catalyzed by $Fe(CO)_5$.[8,10]

The data shown on the rising portion of Figure 1 were taken under conditions of approximately constant illumination. However, the solutions once photolyzed have characteristics of a true thermal catalyst retaining catalytic activity over periods of several hours in the dark. Eventually the solutions lose activity for reasons not clearly understood at present.

The electronic spectrum of the yellow solution resulting from photolysis reveals a broad band system having a band maximum at 408 nm which closely resembles the low-energy ligand field bands (^1A–^1E) typically found with $M(CO)_5L$ (L = ligand) complexes.[5] The IR spectra of the catalyst solutions in the CO-stretching region show two bands at 1970 and 1910 cm^{-1} and a weak band at 1850 cm^{-1}. These bands can be assigned to $W(CO)_6$ (ν 1975 cm^{-1} in a 1-butanol–water mixture[4]) and the $HCO_2W(CO)_5^-$ anion; literature values of $\nu(CO)$[11] for Ppn $W(CO)_5HCO_2$ are 1900 (s), 1837 (m), 2060 cm^{-1} (w) in CH_2Cl_2. This suggests that the photochemical conversion of $W(CO)_6$ to $W(CO)_5$ is not complete under the conditions of these experiments.

A series of control experiments were performed by using solutions of $W(CO)_6$ in tetrahydrofuran (THF). Each of these experiments consisted of determining the rate of H_2 production after combining separately prepared solutions of (a) $W(CO)_6$ (0.120 mmol) in 50 mL of THF and (b) sodium formate (40 mmol) dissolved in 150 mL of a 33:67 water–2-ethoxyethanol (v/v) solvent mixture. These experiments were performed in a closed system under argon. The first of these experiments was carried out entirely in the dark. Here the THF solution of $W(CO)_6$, maintained at room temperature, was added to a hot (T = 62 °C) solution of sodium formate in the ethoxyethanol–water mixture. The rate of H_2 production from this final mixture was very low (0.17 day^{-1}). In the second experiment, the $W(CO)_6$–THF solution was photolyzed by sunlight at room temperature prior to mixing. The two solutions were combined as before and maintained in the dark at T = 62 °C. The hydrogen production rate from the final mixture was found to be 13 day^{-1} corresponding to a 77-fold enhancement in rate. The third experiment differed from the second only in that the solutions were mixed and maintained in sunlight. The H_2 production following mixing (14 day^{-1}) was substantially the same as that found in the second experiment of this series. In each case no H_2 was produced prior to mixing, although small amounts of CO were detected immediately following illumination of the $W(CO)_6$–THF solutions. On the basis of the preliminary experiments reported here, it can be concluded that (a) the hydrogen and carbon dioxide produced in these reactions result from the decomposition of formate ion; (b) $W(CO)_6$ is a precursor to the catalytically active $W(CO)_5$ which enters a catalytic cycle originally proposed for the water gas shift reaction (eq 3–6) at eq 3; and (c) as shown by others,[12,13] the photolytic decomposition of a catalyst precursor can provide a very effective means for promoting activity of certain catalytic systems.

Acknowledgment. We express appreciation for the support provided by the Division of Basic Energy Sciences of the U.S. Department of Energy under Contract EY-76-S-09-0933.

---

[7] Gas-phase concentrations of CO_2 and H_2 produced in equimolar quantities in solution will not necessarily be equal due to differences in the liquid-phase solubilities of these two gases. With methanol–water mixtures, the gas-phase concentration of CO_2 is less than that for H_2 due to the relatively high solubility of CO_2 in the liquid phase.[4,8] Laine, Rinker, and Ford report that the gas-phase concentrations of CO_2 and H_2 are equal for a similar reaction carried out over mixtures of 2-ethoxyethanol and water suggesting that the solubility of CO_2 is relatively low in this latter solvent system.

(8) King, A. D., Jr.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028.

(9) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 252.

(10) Kang, H.; Mauldin, C. H.; Cole, T.; Slegeir, W.; Cann, K.; Pettit, R. *J. Am. Chem. Soc.* **1977**, *99*, 8323.

(11) Schlientz, W. J.; Lavender, Y.; King, R. B.; Ruff, J. K. *J. Organomet. Chem.* **1971**, *33*, 357.

(12) Nasielski, J.; Kirsch, P.; Wilputte-Steinert, L. *J. Organomet. Chem.* **1971**, *27*, C13.

(13) Wrighton, M.; Schroeder, M. A. *J. Am. Chem. Soc.* **1973**, *95*, 5764.

Isolation and Characterization of the First Host Recognition Substance for Parasitic Angiosperms

David G. Lynn,*[†] John C. Steffens,[‡] Vinayak S. Kamut,[†]
David W. Graden,[†] Jeffrey Shabanowitz,[†] and
James L. Riopel*[§]

Departments of Chemistry and Biology
University of Virginia
Charlottesville, Virginia 22901

Received December 15, 1980

Parasitic angiosperms develop a specialized organ for host attachment termed the haustorium. This organ becomes both a morphological and a physiological bridge between the host and parasite. We (Riopel and Musselman)[1,2] and others[3] have shown that parasitic angiosperms cultured in the absence of host roots develop few or no haustoria. Initiation is achieved rapidly with exposure of *Agalinis purpurea* (Scrophulariaceae) to host root exudate or gum tragacanth, a commercially available exudate of *Astragalus spp.* (Leguminosae). Haustorial formation is central to the parasitic attack and is common to virtually all parasitic angiosperms.[4] Using haustorial initiation as a bioassay, we wish to describe the rapid, small-scale isolation and characterization of the first host recognition substance.

In order to understand the nature of the compounds responsible for host recognition, we have concentrated our efforts on gum tragacanth. Soxhlet extraction of the gum (250 g) serially with hexane (1.5 L) and ether (1.5 L), each for 24 h, resulted in an activity-rich ether fraction which was concentrated to yield 600 mg of crude material. Partition between CCl_4 and 50% aqueous

---

[†] Department of Chemistry.

[‡] Departments of Chemistry and Biology.

[§] Department of Biology.

(1) Riopel, J. L.; Musselman, L. J. *Am. J. Bot.* **1979**, *66*, 570–575.

(2) Riopel, J. L. "Proceedings of the Second Symposium on Parasitic Weeds"; Musselman, L. J., Worsham, A. D., Eplee, R. E., Eds.; North Carolina State University: Raleigh, NC, 1979; pp 165–173.

(3) Atsatt, P. R.; Hearn, T. E.; Nelson, R. L.; Heineman, R. T. *Ann. Bot.* (*London*) **1978**, *42*, 1177–1184.

(4) Kuijt, J. *Ann. Rev. Phytopathol.* **1977**, *17*, 91–118.

0002-7863/81/1503-1868$01.25/0