The Role of Rhodium Porphyrins in the Photoassisted Formation of Formaldehyde and Methanol from Hydrogen and Carbon Monoxide

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Benzene solutions of rhodium octaethylporphyrin dimer in the presence of H_2 and CO catalytically produce formaldehyde and methanol when irradiated with 300 nm light.

The metal–metal bonded dimers of rhodium octaethyl- and tetraphenyl-porphyrin are at present the only reported transition metal compounds that react with H_2 and CO to produce observable equilibrium quantities of metalloformyl species[1] [equations (1) and (2)]. We have been exploring strategies to utilize this presently unique feature of rhodium porphyrin chemistry in the production of organic molecules from H_2 and CO. We report that irradiation of benzene solutions containing rhodium octaethylporphyrin (OEP) dimer, hydrogen, and carbon monoxide [$\lambda \geqslant 300$ nm, $T = 298$ K, $P(H_2) + P(CO) < 1$ atm] produces observable quantities of formaldehyde (Figure 1). At slightly elevated temperatures (353 K), methanol is produced catalytically (Figure 2).
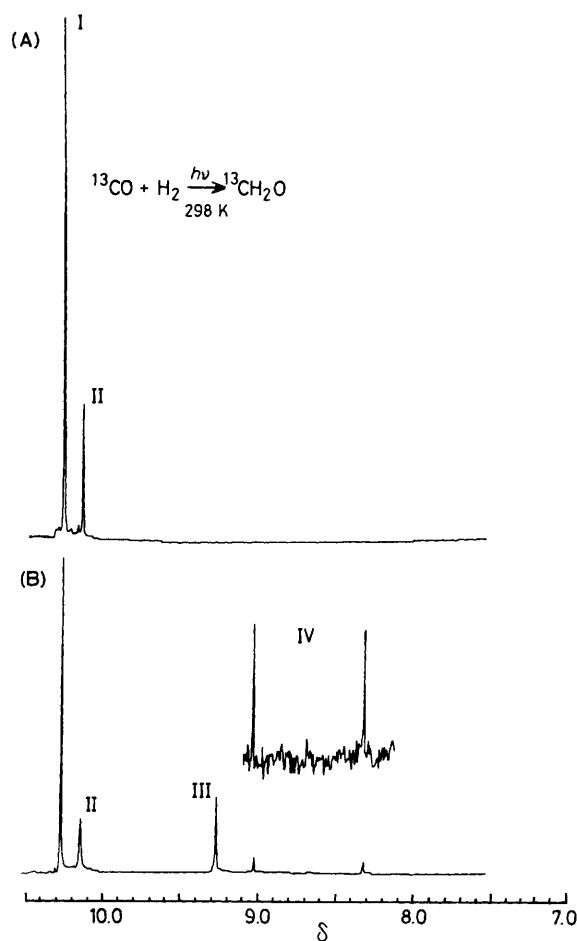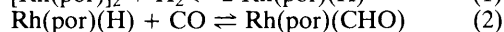
$$[Rh(por)]_2 + H_2 \rightleftharpoons 2\ Rh(por)(H) \qquad (1)$$
$$Rh(por)(H) + CO \rightleftharpoons Rh(por)(CHO) \qquad (2)$$

Formation of H_2CO probably occurs *via* homolytic cleavage of the rhodium–carbon bond in Rh(OEP)(CHO), and subsequent abstraction of a hydrogen atom from Rh(OEP)(H) [equations (3)—(5)]. Reactions (1)—(5) describe a catalytic cycle for the photopromoted formation of H_2CO from H_2 and CO. The proposed mechanism for this cycle is consistent with the previously observed photolytic rhodium–carbon bond dissociation in Rh(OEP)(CH$_3$)[2] and the use of Rh(OEP)(H) as a hydrogen atom source in radical chain mechanisms.[3]

In one representative experiment, a benzene solution containing [Rh(OEP)]$_2$, H_2 (1.0 × 10^{-3} M), and CO (2.6 × 10^{-3} M)† in a sealed n.m.r. tube was allowed to react thermally (298 K) to form equilibrium concentrations of Rh(OEP)(H)
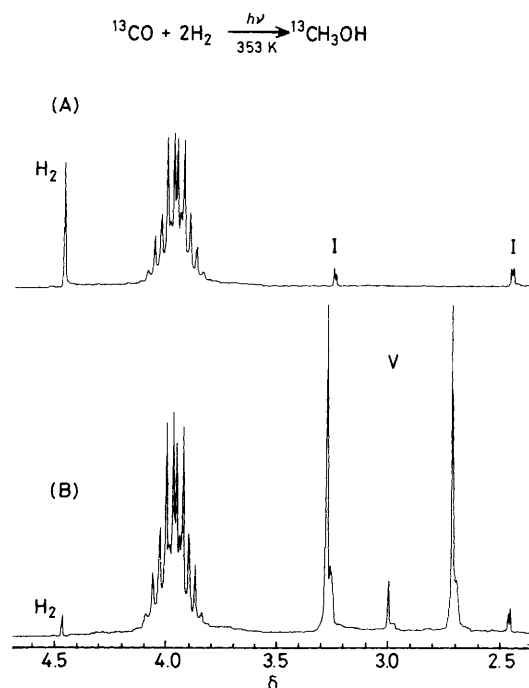
$$^{13}CO + 2H_2 \xrightarrow[353\ K]{h\nu} {}^{13}CH_3OH$$

Figure 2. ^{1}H N.m.r. spectra of rhodium octaethylporphyrin species in C$_6$D$_6$ under H$_2$ and ^{13}CO. I = Rh(OEP)(^{13}CHO); V = ^{13}CH$_3$OH. (A): Thermal equilibrium [$T = 353$ K; $P(H_2) + P(^{13}CO) = 600$ Torr]. (B): Products from photolysis of solution (A) ($\lambda \geqslant 300$ nm; $t = 36$ h; $T = 353$ K); $\delta(^{13}CH_3OH)$ 2.99; $J(^{13}C–^1H)$ 140 Hz.
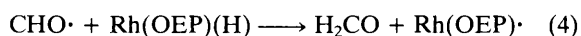
Figure 1. ^{1}H N.m.r. spectra of rhodium octaethylporphyrin species in C$_6$D$_6$ under H$_2$ and ^{13}CO. I = Rh(OEP)(^{13}CHO); II = Rh(OEP)(H); III = [Rh(OEP)]$_2$; IV = ^{13}CH$_2$O. (A): Thermal equilibrium [$T = 298$ K; $P(H_2) + P(^{13}CO) = 600$ Torr]. (B): Products from photolysis of solution (A) ($\lambda \geqslant 300$ nm; $t = 45$ min; $T = 298$ K); $\delta(^{13}CH_2O)$ 8.68; $J(^{13}C–H)$ 176 Hz.

and Rh(OEP)(CHO). The sample was then irrradiated in a Rayonet model RMR-400 reactor utilizing a single 3000 Å source for 45 min at 298 K. Under these conditions, a steady-state concentration of H_2CO (3.7 × 10^{-5} M) was measured by integration of the ^1H n.m.r. spectrum (H_2CO, δ 8.68; H_2, δ 4.46). The dissociation of H_2CO into H_2 and CO is known to occur photochemically,[4] and has also been independently observed as a thermal reaction catalysed by [Rh(OEP)]$_2$.[5] When irradiation was terminated, the H_2CO was depleted by thermal back reaction with [Rh(OEP)]$_2$, and the initial equilibrium concentrations of Rh(OEP)(H) and Rh(OEP)(CHO) were re-established. The equilibrium molar concentration of H_2CO under these conditions is estimated from gas phase thermodynamic values to be ~1 × 10^{-9} M,‡ which is too small to be observed by ^1H n.m.r. spectroscopy.

$$Rh(OEP)(CHO) \xrightarrow{h\nu} Rh(OEP)\cdot + CHO\cdot \quad (3)$$

$$CHO\cdot + Rh(OEP)(H) \longrightarrow H_2CO + Rh(OEP)\cdot \quad (4)$$

$$2\ Rh(OEP)\cdot \longrightarrow [Rh(OEP)]_2 \quad (5)$$
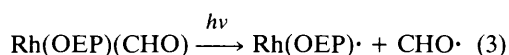
A similar experiment performed at 353 K resulted in catalytic formation of methanol. Conversion of ^{13}CO and H_2 into $^{13}CH_3OH$ was obtained by extended periods (36 h) of irradiation [δ_H $^{13}CH_3OH$ 2.99; δ_c $^{13}CH_3OH$ 50.2; $J(^{13}C-^1H)$ 140 Hz]. (Figure 2). One pathway for the production of methanol results from formation of Rh(OEP)(CH$_2$OH) [equation (6)], and subsequent intermolecular reductive

elimination of CH_3OH from reaction of Rh(OEP)(CH$_2$OH) and Rh(OEP)(H) [equation (7)]. Reactions (6) and (7) have been independently observed as thermal reactions.[6,7] Elevated temperature (>343 K) has been shown to be required for reaction (7) to occur at a measurable rate.[7]

$$Rh(OEP)(H) + CH_2O \rightleftharpoons Rh(OEP)(CH_2OH) \quad (6)$$

$$Rh(OEP)(CH_2OH) + Rh(OEP)(H) \rightarrow [Rh(OEP)]_2 + CH_3OH \quad (7)$$
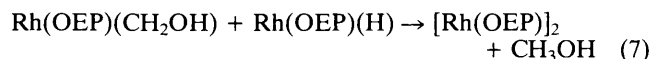
We are currently measuring product quantum yields at various wavelengths, investigating the chemical trapping of H_2CO, and continuing mechanistic studies for each step in the proposed catalytic cycle [reactions (1)—(7)].

‡ $H_2(g) + CO(g) \rightleftharpoons H_2CO(g)$; $\Delta H°\ 298 = -5.5$ kJ/mol, $\Delta S°\ 298 = -109.4$ J mol^{-1} K^{-1}.

References

1 B. B. Wayland and B. A. Woods, *J. Chem. Soc., Chem. Commun.*, 1981, 700.
2 M. Hoshino, K. Yasufuku, H. Seki, and H. Yamazaki, *J. Phys. Chem.*, 1985, **89**, 3080.
3 R. S. Paonessa, N. C. Thomas, and J. Halpern, *J. Am. Chem. Soc.*, 1985, **107**, 4333.
4 C. Cheng, P. Ho, C. B. Moore, and M. B. Zughul, *J. Phys. Chem.*, 1984, **88**, 296.
5 B. B. Wayland *et al.*, unpublished results.
6 B. B. Wayland, B. A. Woods, and V. M. Minda, *J. Chem. Soc., Chem. Commun.*, 1982, 634.
7 S. L. Van Voorhees and B. B. Wayland, *Organometallics*, 1985, **4**, 1887.