# Photosensitized Cleavage of Acetylene to Methane

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Photosensitized reductive cleavage of acetylene to methane is accomplished in an aqueous solution that includes $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) as sensitizer, triethanolamine as electron donor, and an $[RuL_5(H_2O)]^{2+}$ complex that acts as electron acceptor and catalyst in the process.

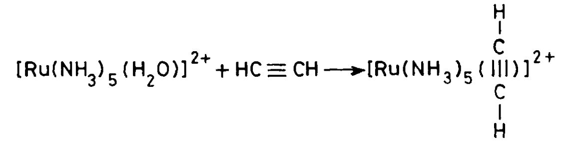
Application of photoinduced electron-transfer reactions for $CO_2$ or $N_2$ fixation is of substantial interest.[1] Nitrogenase, the dinitrogen fixation enzyme, acts non-specifically towards substrates that are isoelectronic with nitrogen.[2] For example, acetylene is reduced to ethylene by nitrogenase together with the nitrogen fixation process. Here we report on the photosensitized reductive cleavage of acetylene to methane in the presence of $Ru^{II}$-complexes as fixation catalysts. These systems might offer an insight to the development of nitrogen fixation systems.

The systems were composed of an aqueous solution (pH 10) that includes tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3]^{2+}$ ($1 \times 10^{-4}$ M) as sensitizer, triethanolamine ($1 \times 10^{-2}$ M) as electron donor, and one of the following $Ru^{III}$ co-ordination compounds ($2 \times 10^{-3}$ M), $[Ru(NH_3)_5Cl]^{2+}$, $[RuCl_5(H_2O)]^{2-}$, $[Ru(edta)]^-$, and $[Ru(ox)_2(H_2O)_2]^-$ ($H_4$edta = ethylenediaminetetra-acetic acid; $H_2$ox = oxalic acid), as electron acceptor and catalyst for acetylene fixation. The deaerated system was flushed with acetylene, and illuminated with visible light ($\lambda > 400$ nm) in a glass cuvette. Methane is formed

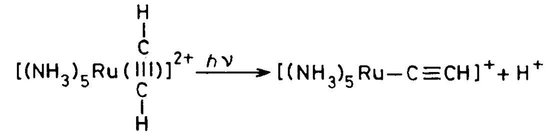
$$HC\equiv CH + 6H^+ + 6e^- \longrightarrow 2CH_4 \qquad (1)$$

$$^*[Ru(bpy)_3]^{2+} + [Ru(NH_3)_5Cl]^{2+} \longrightarrow [Ru(bpy)_3]^{3+} + [Ru(NH_3)_5Cl]^+ \qquad (2)$$

$$[Ru(NH_3)_5Cl]^+ + H_2O \longrightarrow [Ru(NH_3)_5(H_2O)]^{2+} + Cl^- \qquad (3)$$



$$[Ru(NH_3)_5(H_2O)]^{2+} + HC\equiv CH \longrightarrow [Ru(NH_3)_5(\overset{\substack{H\\|\\C}}{\underset{\substack{C\\|\\H}}{|||}})]^{2+} \qquad (4)$$



$$[(NH_3)_5Ru(\overset{\substack{H\\|\\C}}{\underset{\substack{C\\|\\H}}{|||}})]^{2+} \xrightarrow{h\nu} [(NH_3)_5Ru{-}C\equiv CH]^+ + H^+ \qquad (5)$$

$$5[Ru(NH_3)_5(H_2O)]^{2+} + [(NH_3)_5Ru{-}C\equiv CH]^+ + 6H^+ \longrightarrow [6Ru(NH_3)_5(H_2O)]^{3+} + 2CH_4 \qquad (6)$$

in the system† and the variation in its formation with time is displayed in Figure 1. No methane is formed in the absence of the electron acceptor, the sensitizer, triethanolamine, or acetylene. This implies that all the components participate in the photocleavage of acetylene to methane, a reaction that involves six electrons in the reduction process [equation (1)].

Several attempts to elucidate some of the mechanistic aspects of this process have been conducted with $[Ru(NH_3)_5Cl]^{2+}$ as electron acceptor.‡ Illumination of the system under argon instead of acetylene results in the photoreduction[3] of $[Ru(NH_3)_5Cl]^{2+}$ followed by aquation to give $[Ru(NH_3)_5(H_2O)]^{2+}$ [equations (2) and (3)]. The latter complex binds acetylene in a 'side-on' complex[4] [equation (4)] and therefore we assign this complex as the primary intermediate in the photocleavage of acetylene. {The i.r. spectrum of $[Ru(NH_3)_5(HC\equiv CH)]^{2+}$ shows a stretching band at 1775 $cm^{-1}$ consistent with a 'side-on' acetylene configuration}. The complex $[Ru(NH_3)_5(HC\equiv CH)]^{2+}$ was prepared chemically by the reaction of $[Ru(NH_3)_5(H_2O)]^{2+}$ and acetylene[4] and was introduced into the photochemical system that included the sensitizer, $[Ru(bpy)_3]^{2+}$, and triethanolamine. Evolution of methane was observed upon illumination, suggesting that $[Ru(NH_3)_5(HC\equiv CH)]^{2+}$ is indeed an intermediary species in the process. Nevertheless, further observations imply that the process involves additional intermediates. Addition of zinc amalgam as reducing agent to an aqueous solution of $[Ru(NH_3)_5(HC\equiv CH)]^{2+}$ does not yield methane. Yet, prior illumination ($\lambda > 400$ nm) of the $[Ru(NH_3)_5(HC\equiv CH)]^{2+}$ aqueous solution followed by the addition of zinc amalgam leads to the formation of methane. This suggests that the complex $[Ru(NH_3)_5(HC\equiv CH)]^{2+}$ undergoes photochemical activation to a species capable of evolving methane.

Upon illumination of the aqueous $[Ru(NH_3)_5(HC\equiv CH)]^{2+}$ solution a new complex is formed exhibiting a stretching band at 1930 $cm^{-1}$ in the i.r. spectrum. This stretching band is characteristic[5,6] of an acetylenic bond in a σ-acetylene metal configuration $[(NH_3)_5Ru{-}C\equiv CH]^+$. Thus, we attribute the photochemical activation process involved in the reaction to a π–σ acetylene rearrangement [equation (5)]. Similar photochemical rearrangements have been previously reported with other metal–acetylene complexes.[7]

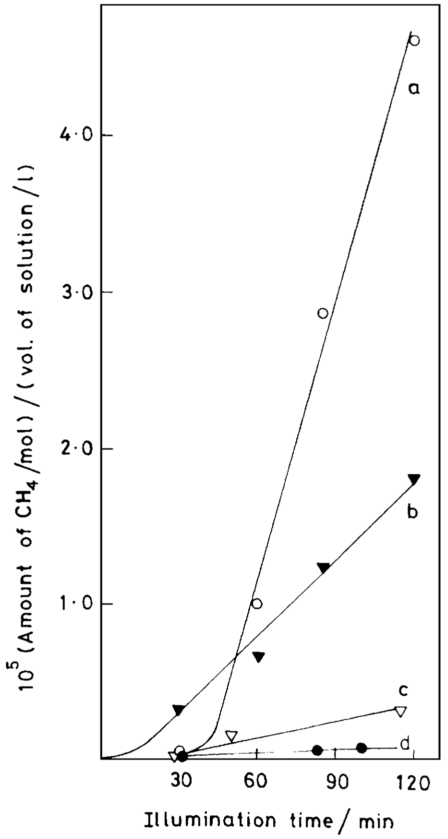


**Figure 1.** Rate of methane evolution from acetylene as a function of illumination time: (a) with $[Ru(NH_3)_5Cl]^{2+}$; (b) with $[Ru(edta)]^-$; (c) with $[RuCl_5(H_2O)]^{2-}$; (d) with $[Ru(ox)_2(H_2O)_2]^-$. In all experiments the concentration of the $Ru^{III}$ complex was $2 \times 10^{-3}$ M; of triethanolamine was $1 \times 10^{-2}$ M; and of the sensitizer, $[Ru(bpy)_3]^{2+}$, $1.1 \times 10^{-4}$ M.

Introduction of photogenerated $[Ru(NH_3)_5(H_2O)]^{2+}$ to an aqueous solution of the photoactivated acetylide complex $[(NH_3)_5Ru{-}C\equiv CH]^+$ results in the formation of methane. This suggests that the complex $[(NH_3)_5Ru{-}C\equiv CH]^+$ offers a charge relay that accumulates the electrons transferred by the

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† Gases were analysed by gas chromatography, Poropak N column. 2 Moles of $CH_4$ are formed per mole of $[Ru^{II}L_5(H_2O)]^{2+}$.

‡ The quenching rate constants ($10^{-9} \times k_q/dm^3\ mol^{-1}\ s^{-1}$) of $^*[Ru(bpy)_3]^{2+}$ by the electron acceptors are: with $[Ru(NH_3)_5Cl]^{2+}$, 2.7; with $[RuCl_5(H_2O)]^{2-}$, 8.2 ± 0.6; with $[Ru(edta)]^-$, 4.9 ± 0.5; with $[Ru(ox)_2(H_2O)_2]^-$, 0.95 ± 0.1.

photogenerated $[Ru(NH_3)_5(H_2O)]^{2+}$ and activates acetylene towards the photocleavage process [equation (6)].

The mechanism for the conversion of the acetylide ligand into methane is not known at present. Recently, Meyer *et al.* have reported[8] on the interesting cleavage of phenylacetylene to toluene and CO in the presence of $Ru^{II}$ and $Os^{II}$ complexes. This metal-promoted thermal hydration has been shown to proceed *via* the intermediate benzyl–ruthenium(II) complex. In the present system, the acetylide complex $[Ru(NH_3)_5{-}C{\equiv}CH]^+$ does not undergo a similar thermal hydration process to give methane, and introduction of reduction equivalents in the form of photogenerated $[Ru(NH_3)_5(H_2O)]^{2+}$ is required. Nevertheless, it seems reasonable to assume that alkyl,[8] vinylidene, and carbene complexes[9] might participate as intermediates in the photocleavage of acetylene to methane.

We have also examined the similar reaction using substituted acetylenes. With prop-1-yne as substrate photocleavage led to methane and ethane. With but-1-yne, methane and propane were formed. These results clearly demonstrate that the carbon–carbon triple bond is reductively photocleaved to give the respective alkanes. The similar process is prevented, however, when but-2-yne is used as substrate, and no reduction products are obtained. This result is attributed to the lack of an acetylenic hydrogen bond on the substrate capable of undergoing the previously discussed $\pi$–$\sigma$ acetylenic bond rearrangement. Similar photocleavage of acetylene to methane is accomplished when *meso*-tetramethylpyridinium zinc-porphyrin is used as sensitizer instead of $[Ru(bpy)_3]^{2+}$.

In conclusion, we have demonstrated that acetylene and terminal acetylenes undergo photosensitized cleavage to give the respective alkanes. In view of the similarities of the acetylene and dinitrogen (N≡N) bonds, and since the formation of $[Ru(NH_3)_5(N{\equiv}N)]^{2+}$ is well established,[10] we believe that related processes might lead to the photochemical fixation of nitrogen to ammonia.

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## References

1 A. J. Bard, *Science*, 1980, **90**, 138.
2 G. N. Schrauzer, in 'New Trends in the Chemistry of Nitrogen Fixation,' eds. J. Chatt, L. M. de Camara Pina, and R. L. Richards, Academic Press, London, 1980, p. 105.
3 G. Navon and N. Sutin, *Inorg. Chem.*, 1974, **13**, 2159.
4 H. Lehman, K. J. Schenk, G. Ghapuis, and A. Ludi, *J. Am. Chem. Soc.*, 1979, **101**, 6197.
5 P. J. Kim, H. Masai, K. Sonogashira, and M. Hagihara, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 181.
6 A. Davison and J. P. Selogue, *J. Am. Chem. Soc.*, 1978, **100**, 7763.
7 A. B. Antonova, N. E. Kolobova, P. V. Petrosky, B. V. Lokshin, and N. S. Obezyuk, *J. Organomet. Chem.*, 1977, **137**, 55.
8 B. P. Sullivan, R. S. Smythe, E. M. Kober, and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4701.
9 M. I. Bruce and A. G. Swincer, *Adv. Organomet. Chem.*, 1983, **22**, 60.
10 A. E. Shilov, A. K. Shilova, E. F. Kvashina, and T. A. Vorontsova, *Chem. Commun.*, 1971, 1570; D. F. Harrison, E. Weissberger, and H. Taube, *Science*, 1968, **159**, 320.