

Dihydrogen Evolution by Photolysis of $\text{HFe}(\text{CO})_4^-$ and the Photoassisted Water Gas Shift Reaction: a Possible Dinuclear Reductive Elimination Mechanism

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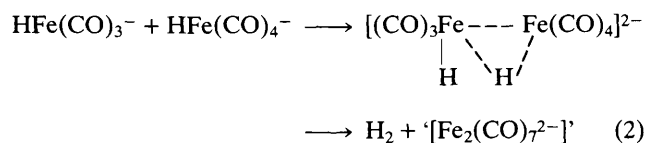
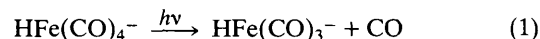
The photolysis of $\text{HFe}(\text{CO})_4^-$ results in the evolution of a 1 : 1 mixture of H_2 and CO under Ar and assists the water gas shift reaction under 1 atm pressure of CO; a suggested mechanism involves the dinuclear reductive elimination of H_2 following the photolytic extrusion of CO from $\text{HFe}(\text{CO})_4^-$.

Although the photochemistry of transition-metal hydrides has been well documented,¹ little is known on the photochemical behaviour of anionic complexes,^{2,3} particularly anionic monohydridocarbonyl complexes which are important species in a variety of catalytic and stoichiometric reactions.^{4,5} We now report that the photolysis of $\text{HFe}(\text{CO})_4^-$ results in the evolution of H_2 unlike those of $\text{HFe}_2(\text{CO})_8^-$ and $\text{HFe}_3(\text{CO})_{11}^-$, thus assisting the water gas shift reaction under 1 atm pressure of CO.

The preparation of $\text{HFe}(\text{CO})_4^-$ was carried out conventionally by *in situ* reactions of $\text{Fe}(\text{CO})_5$ with 3 equiv. of NaOH or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and, in appropriate cases, according to Collman's method.⁶ Figure 1 shows the catalytic evolution of H_2 by irradiation of a thoroughly deaerated solution of $\text{HFe}(\text{CO})_4^-$ with a tungsten-halogen lamp (500 W) under an atmospheric pressure of CO at room temperature. After 40 h irradiation, the amount of CO_2 formed was determined to be ~95% that of the H_2 formed, and $\text{HFe}(\text{CO})_4^-$ mostly survived with $\leq 5\%$ decomposition. *N,N*-Dimethylformamide or tetrahydrofuran (THF) were found to be favourable as solvents, but substantial decomposition of $\text{HFe}(\text{CO})_4^-$ occurred in acetonitrile or methanol.

The photocatalytic evolution of H_2 is of mechanistic interest, since the general pathway in the photochemistry of monohydridocarbonyl complexes is *via* loss of CO or other ligands^{1,7} without H_2 evolution, except in a few cases.⁸ The photolysis of $\text{HFe}(\text{CO})_4^-$ under Ar was found to give a 1 : 1 mixture of H_2 and CO in 9 : 1 THF- H_2O and *even in dry THF* the reaction proceeded with a similar efficiency. Moreover, the photolysis of $^2\text{HFe}(\text{CO})_4^-$ gave ~95% isotopically pure $^2\text{H}_2$ in 9 : 1 THF- H_2O or a 9 : 3 : 1 mixture of $^2\text{H}_2$, $^2\text{H}^1\text{H}$, and

$^1\text{H}_2$ in THF, while little $^2\text{H}_2$ was formed from $^1\text{HFe}(\text{CO})_4^-$ in $[^2\text{H}_8]\text{THF}$. Evidently, the major direct source of the H_2 formed is neither H_2O nor THF, but $\text{HFe}(\text{CO})_4^-$. These observations can be reasonably interpreted in terms of the dinuclear reductive elimination of H_2 following the photolytic extrusion of CO from $\text{HFe}(\text{CO})_4^-$ (equations 1 and 2).⁹



Quantum yields for the H_2 evolution in 9 : 1 THF- H_2O were found to be 0.08 ± 0.002 at 366 nm ($[\text{HFe}(\text{CO})_4^-] = 0.1 \text{ mol dm}^{-3}$) and 0.14 ± 0.01 at 313 nm ($[\text{HFe}(\text{CO})_4^-] = 0.05 \text{ mol dm}^{-3}$) under either an Ar or CO atmosphere as well as in the presence or absence of PPh_3 (0.15 mol dm^{-3}). It appears that equation (2) is much faster than a reaction of $\text{HFe}(\text{CO})_3^-$ with dissolved CO or PPh_3 . The wavelength dependence might reflect the involvement of different electronic transitions in the end absorption at longer wavelength.

I.r. and u.v.-visible absorption spectra of the photolysates revealed no definite absorption assignable to known iron carbonyl complexes other than $\text{HFe}_3(\text{CO})_{11}^-$ in a small amount, indicating that the supposed product, $[\text{Fe}_2(\text{CO})_7]^{2-}$, undergoes further reactions to give higher clusters. However, the photolysis in the presence of PPh_3 gave $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ in ~80% isolated yield based on the H_2

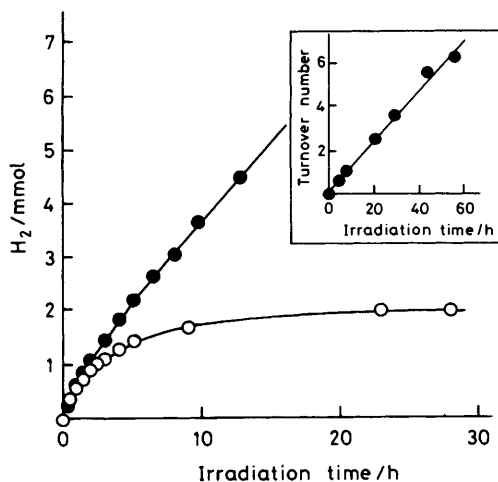
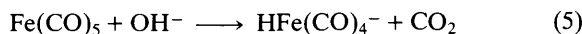
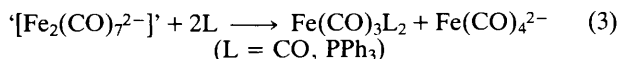


Figure 1. Evolution of H₂ by the photolysis of HFe(CO)₄⁻ under 1 atm pressure of CO (solid circles) or under Ar (open circles) at room temperature; HFe(CO)₄⁻ was generated by an *in situ* reaction of Fe(CO)₅ (3.4 mmol) with DBU (10 mmol) in 9:1 (v/v) *N,N*-dimethylformamide–water (50 cm³). The graph insert shows a plot of mmol H₂ formed per mmol HFe(CO)₄⁻ used (turnover numbers) vs. irradiation time.

formed, an expected product arising from the capture of the Fe(CO)₃ fragment in '[Fe₂(CO)₇²⁻]' by PPh₃ (equation 3). Indeed, no i.r. absorption of Fe(CO)₄(PPh₃) (2050, 1773, and 1940 cm⁻¹) was detected at all throughout the entire course of the photolysis. If a similar reaction efficiently occurs with CO in equation (3) (L = CO), the catalytic cycle of the photoassisted water gas shift reaction under CO can thus be completed *via* equations (4) and (5).



In contrast to HFe(CO)₄⁻, it was confirmed that HFe₃(CO)₁₁⁻ is totally incapable of photocatalysing the H₂

evolution under similar conditions.² Although the photocatalytic evolution of H₂ occurred with NaHFe₂(CO)₈¹⁰ under CO only in the presence of NaOH or DBU, i.r. spectra demonstrated that the true photocatalyst is HFe(CO)₄⁻ formed by rapid declusterification with CO¹⁰ followed by reaction of the Fe(CO)₅ fragment with base, equation (5). Indeed, the photolysis of this dinuclear complex under Ar resulted in the exclusive formation of CO with little evolution of H₂.

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