

Figure 1. Decays of absorption signals of (a) I^- at 510 nm and (b) II^+ at 606 nm following irradiation for 30 s at 450 nm of a solution containing 2×10^{-5} M I , 2.2×10^{-3} M MeODMA, and 1×10^{-4} M II . Path length = 4 cm; i.p. = irradiation period.

rate constant $k_2 = (1.2 \pm 0.2) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The two initial electron-transfer products may react in a reverse-electron-transfer reaction regenerating the ground-state species, (eq 3) or in the presence of II , the MeODMA^+ may oxidize II to II^+ via reaction 4. On addition of sufficient quantity of II to scavenge MeODMA^+ the principle final electron-transfer products are I^- and II^+ which would then react back via reaction 5.

The disappearance of the long-lived electron-transfer products I^- and II^+ could be traced by observing the decays of their optical absorptions at 510 and 606 nm, respectively (see Figure 1) following 30-s irradiation of the total photochemical system in aqueous solution by light of wavelength 450 nm. The absorptions are found to decay in minutes and follow good second-order kinetics. The visible absorption spectrum of the solution before irradiation and several hours after leaving the irradiated solution in the dark were identical indicating the overall regeneration of the ground-state species. The decays are therefore attributed to reaction 5, and assuming that the electron-transfer products possess absorption spectra similar to their monomeric analogues¹⁵ then the rate constant k_3 was estimated to be $(1.5 \pm 0.2) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. This value may be compared to the known rate constant for the electron-transfer reaction between $\text{Ru}(\text{bpy})_3^+$ and the cation radical of N,N,N',N' -tetramethyl-*p*-phenylenediamine of $5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile solution.¹⁶ This represents a factor of inhibition of more than 5 orders of magnitude, which, even after accounting for the change in solvent, is a dramatic degree of retardation. It should be noted that in most photochemical systems studied until now factors of inhibition of the back reaction of usually about 1–2 orders of magnitude have been observed on adding microenvironments such as polyelectrolytes,^{5–12} micelles,¹ vesicles,² microemulsions,³ or charged colloids⁴ to a photochemical system. It is also noted that irradiation of the photochemical system described for many minutes or on repeating the irradiation several times after allowing the electron-transfer products to decay back appears to lead to no change in the final absorption spectrum suggesting that very little side reaction occurs in the system which may be cycled many times. Quantitative measurements concerning the cycling of the system are currently being undertaken.

Isolating the final electron products in separate microenvironments thus appears to be very promising in allowing very high

efficiencies of energy storage by the dramatic inhibition of the back-electron-transfer reaction. It is now hoped that useful chemical reactions yielding synthetic fuels will now be able to compete successfully with the impaired back reaction.

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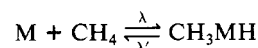
Interactions of Atomic and Molecular Iron with Methane in an Argon Matrix

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In 1979, the first direct insertion of a "ligand-free" metal atom into a carbon–hydrogen bond was reported.¹ Subsequently, it was demonstrated that the first-row late transition metals, with the exception of nickel, will undergo photoinsertion into one of the carbon–hydrogen bonds of methane to yield the methylmetal hydrides, CH_3MH .² Activation of carbon–hydrogen bonds of higher alkanes by photoexcited metal atoms has also been observed in inert gas and neat matrices.^{3,4} The photochemical reaction⁵ between a copper atom and a methane molecule in a neat matrix initially leads to the insertion of the metal atom into a carbon–hydrogen bond of methane followed by disproportionation of this reaction intermediate into CuCH_3 and H and CuH and CH_3 . In the case of the reaction of monatomic iron or manganese with methane and hydrogen, Ozin et al.^{6–8} have shown that these systems undergo photoreversible oxidative addition/reductive elimination reactions



where $\lambda = 300$ (Fe) or 285 nm (Mn) and $\lambda' = 420$ (Fe) or 310 nm (Mn).

In this paper we wish to report on the first observation of a ligand-free metal methane complex in an inert gas matrix. We will further demonstrate that photoinsertion of a metal atom into the carbon–hydrogen bond of methane occurs via the formation of this hydrogen bonded complex. Diatomic iron was also found to interact with methane to form $\text{Fe}_2(\text{CH}_4)$. Photoinsertion of the diiron into the carbon–hydrogen bond of methane was not observed.

Figure 1 depicts infrared spectra measured at different metal concentrations and obtained when iron and methane were co-

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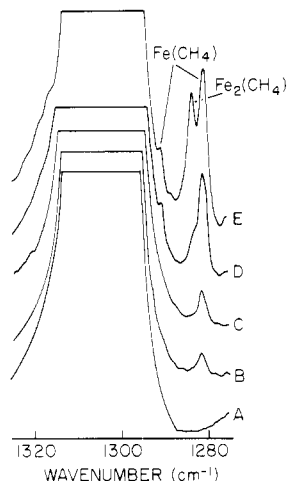


Figure 1. FTIR spectra of Fe/CH₄ in solid argon at 14 K. An iron concentration study. Molar ratio of CH₄:Ar = 5:1000. Molar ratio of Fe:Ar: (A) 0.0:1000; (B) 0.9:1000; (C) 2.1:1000; (D) 5.8:1000; (E) 12.2:1000.

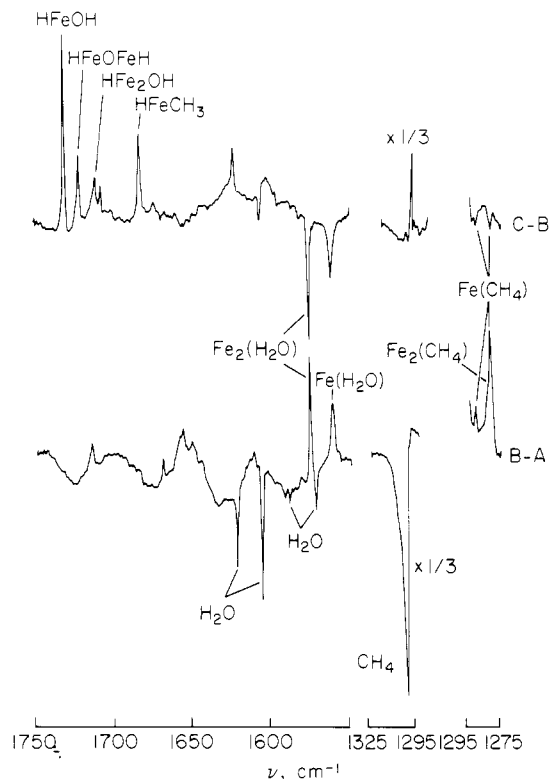


Figure 2. FTIR difference spectra of Fe/CH₄/H₂O reaction and photochemistry in solid argon at 14 K. Molar ratios of Fe:CH₄:H₂O:Ar ~ 5.8:5.1:2.5:1000: (A) without iron; (B) without photolysis; (C) after 30-min photolysis (280 nm < λ < 360 nm).

condensed in excess argon for 30-min periods. New product bands appeared at 1281.7, 1284.1, and 1291.1 cm⁻¹. Under low metal dispersion conditions (Fe/Ar ~ 1–20/10⁴), the peak at 1281.7 cm⁻¹ was the only observable absorption. Both this peak and the small shoulder at 1291.1 cm⁻¹ decreased in intensity when ultraviolet radiation from a mercury discharge lamp was shone on the matrix. This reduction in product bands was accompanied by the concomitant growth of the methyliron hydride peaks (Figure 2). The absorption at 1284.1 cm⁻¹ remained unchanged. From the metal concentration and photolysis studies the new absorption bands can be grouped into two sets. The set of bands at 1291.1

Table I. FTIR Measured Frequencies (cm⁻¹) for the ν₄ (f₂) Mode of Free and Perturbed CH₄ and CD₄ in Solid Argon

CH ₄	1305.3	993.6	CD ₄
Fe(CH ₄)	1291.1	984.0	Fe(CD ₄)
	1281.7	974.6	
Fe ₂ (CH ₄)	1284.1	976.8	Fe ₂ (CD ₄)

and 1281.7 cm⁻¹, present under dilute conditions and sensitive to ultraviolet irradiation, was assigned to the methane iron complex Fe(CH₄). The other peak was predominant at high iron concentrations and did not show any photosensitivity to UV irradiation. Hence, it seemed appropriate to assign its measured frequency to the diiron methane complex, Fe₂(CH₄).

No bands assignable to a CH₃Fe₂H species were observed in support of earlier studies.^{2,9} More recently¹⁰ the unreactivity of iron clusters toward methane was again demonstrated in new experiments where reactions would take place at the interface of a dense flow reactor and a molecular beam. No perturbation of the carbon-hydrogen stretching modes of methane was measured for either the mono- or diiron methane complex. The frequency shifts might be so small that these adduct bands are buried under the broad methane absorption (half-band width ~ 30 cm⁻¹). Similar experiments carried out with perdeuteriomethane gave rise to peaks at 974.6 and 984.0 cm⁻¹ and 976.8 cm⁻¹ assignable to Fe(CD₄) and Fe₂(CD₄), respectively. Table I lists the measured frequencies for the mono- and diiron methane complexes along with the unperturbed frequencies of free matrix isolated CH₄ and CD₄ in solid argon.

Figure 2 presents difference spectra reflecting the chemistry and photochemistry of the binary systems Fe/CH₄ and Fe/H₂O in solid argon. No ternary reaction between iron, methane, and water was observed in this matrix. It is interesting to note that the extinction coefficient of the ν₄ mode of CH₄ is reduced dramatically upon complexation with either Fe or Fe₂. Photolysis caused the formation of HFeCH₃ but primarily led to the dissociation of Fe(CH₄) as noted by the growth of the CH₄ peak in Figure 2. The quantum yield of HFeCH₃ was observed to be much higher in a neat matrix^{2,6} where the iron methane complex is totally surrounded by methane molecules in the matrix cage and thus photodissociation does not lead to the depletion of the precursor of the insertion product. No diiron methane insertion product was formed in either an argon or neat matrix in contrast to the results of the Fe/H₂O photochemistry¹¹ where both HFeOH and HFe₂OH were produced.

In the case of the interaction between atomic iron and methane, the triply degenerate ν₄ (f₂) absorption of methane has been split into two peaks indicating a C_{3v} symmetry. The 1281.7-cm⁻¹ absorption may be attributable to the doubly degenerate e mode with the 1291.1-cm⁻¹ peak assigned to the a₁ mode, since the intensity of the former is about double that of the latter. The iron atom may be bonded to one of the hydrogen atoms of methane along the C₃ axis of the molecule, or it may be partially and simultaneously bonded to three hydrogen atoms that occupy the vertices of the base of the CH₃ pyramid. However, one cannot rigorously exclude the possibility that the degeneracy of the ν₄ (f₂) mode has been totally removed due to an iron methane structure of a lower symmetry and that the third expected peak is either too weak and/or hidden under the intense methane absorption.

Future studies will be carried out to investigate the interactions between other transition-metal atoms and clusters with alkanes.

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