

Activation of O–H and C–O Bonds of Methanol by Photoexcited Iron Atoms

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The activation of the O–H and C–O bonds of methanol has been accomplished by photoexcitation of the Fe(MeOH) adduct, formed from the cocondensation of iron–methanol with an excess of argon at 14 K, in the violet (400 nm < λ < 500 nm) and u.v. (280 nm < λ < 360 nm) regions, respectively; prolonged u.v. photolysis leads to the formation of carbon monoxide and hydrogen, an interesting observation in that it apparently represents the reverse of the Fischer–Tropsch process for methanol synthesis.

Since the initial development of the Fischer–Tropsch process for methanol synthesis,¹ many studies have been carried out to determine the nature of the catalytic function of different transition metals in this process. In 1966, Blyholder and Neff² suggested the formation of an alkoxide type intermediate in studies of the adsorption of different alcohols on iron powder. More recently, Benziger and Madix³ studied the reactions of alcohols on an iron surface and showed the formation of the metal alkoxide as a reaction intermediate. Here we report the reaction and photochemistry of methanol with atomic iron in an argon matrix.

Iron atoms, obtained by vaporizing the metal at 1100–1400 °C from an alumina Knudsen cell, were codeposited with methanol and an excess of argon onto a rhodium-plated copper surface at 14 K. The i.r. spectra, measured with an IBM IR98 vacuum Fourier transform spectrophotometer, contained two sets of peaks at 3591.8, 1062.1, 972.2 cm⁻¹ and at 3629.4, 1075.8, 997.5, 996.3 cm⁻¹, which can be attributed to products from the cocondensation of iron and methanol. The former was predominant at low iron dispersion and showed a linear dependence on the metal concentration. The latter appeared at higher iron concentration and grew at a

faster rate than the former with increasing metal concentration. These two sets of peaks were assigned to the adducts, Fe(MeOH) and Fe₂(MeOH), respectively. Only the photolytic behaviour of the monoiron adduct will be discussed in this communication.

Broad band irradiation of the matrix with a mercury lamp using a 500 nm cut-off filter did not have any effect on the monoiron adduct peaks. However, photolysis of the matrix with a 400 nm cut-off filter caused the growth of new peaks in the Fe–H stretching region at 1741.0 cm⁻¹ and the C–H stretching region at 2812.9 cm⁻¹ and the reduction of the Fe(MeOH) peaks as shown in Figure 1. Deuterium labelling studies confirmed the mode assignments of these two peaks to Fe–H and C–H stretching modes, respectively. It is proposed that the complex, Fe(MeOH), when photoexcited in the violet region will rearrange with metal insertion into the O–H bond of methanol. A comparison of the ν (Fe–H) stretching frequency measured for MeOFeH with that reported for HOFeH^{4,5} shows very similar values. The ν (Fe–O) absorption was not detected presumably because it has shifted to the far i.r. region with the heavier methyl group substituting for hydrogen.

Upon u.v. (280 nm < λ < 360 nm) photolysis, metal photoinsertion into the C–O bond of methanol to yield methyliron hydroxide, MeFeOH, was observed as evidenced from new peaks growing at 3744.8 and 687.5 cm⁻¹, shown in Figure 1. The photoinsertion product peaks are located in the O–H and Fe–O stretching regions, respectively. In the case of CD₃OD, CD₃FeOD was formed upon u.v. photolysis, with a ν (O–D) stretching frequency at 2759.6 cm⁻¹ and a ν (Fe–O) stretching frequency at 667.3 cm⁻¹, respectively. A comparison of the frequencies of the O–H and the Fe–O stretching modes of MeFeOH and HOFeH, listed in Table 1, indicates that they are very similar. Thus the substitution of the methyl group for hydrogen seems to have a minimal effect on the frequencies of the HOFe moiety indicating similarity between the interactions of iron and hydrogen, and iron and methyl.

Further photolysis in the u.v. region led to methanol

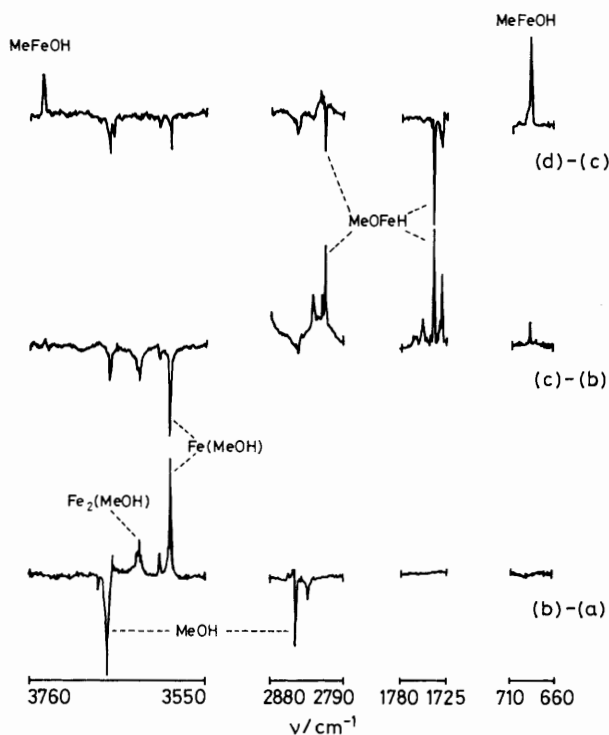


Figure 1. Fourier transform i.r. difference spectra of adducts and photoproducts of the reaction of iron with methanol in solid argon. Molar ratio of Fe:MeOH:Ar 5.3:10.0:1000; (a) no iron; (b) no photolysis; (c) λ > 400 nm, 0.5 h; (d) 280 nm < λ < 360 nm, 1 h.

Table 1. Measured Fourier transform i.r. frequencies (cm⁻¹) of hydroxyiron hydride, methoxyiron hydride, and methyliron hydroxide in solid argon.

Stretching mode	HOFeH ^a	MeOFeH	MeFeOH
O–H	3741.5	—	3744.8
H–Fe	1731.0	1741.0	—
Fe–O	679.8	—	687.5
Stretching mode	DOFeD ^a	CD ₃ OFeD	CD ₃ FeOD
O–D	2757.7	—	2759.6
D–Fe	1246.0	1253.5	—
Fe–O	660.5	—	667.3

^a References 4 and 5.

photodissociation to carbon monoxide and hydrogen as indicated by peaks at 2137.9, 1941.0, and 1660.7 cm^{-1} which are due to free CO, iron monocarbonyl, and iron dihydride, respectively. The peak at 1941.0 cm^{-1} has been assigned to the C–O stretching of an iron carbonyl species since it exhibited a large ^{13}C shift of 43.6 cm^{-1} . The absorption at 1660.7 cm^{-1} shifted to 1204.3 cm^{-1} when CD_3OD was used as the reactant substrate. These frequencies have been recently measured in our laboratory when iron atoms were photoreacted with either hydrogen or deuterium in argon matrices. They have been assigned⁶ to FeH_2 and FeD_2 , respectively. Ozin and McCaffrey⁷ have also measured the i.r. spectra of FeH_2 and FeD_2 in krypton and xenon matrices. There is good agreement between the measured frequencies in argon⁶ and in krypton and xenon⁷ matrices. These observed photoproducts, mainly carbon monoxide, iron carbonyl, and iron dihydride, are apparently derived from subsequent photolysis of MeOFeH since its bands were reduced during u.v. photolysis. MeFeOH was not affected by prolonged u.v. photolysis once it was formed. The formation of carbon monoxide and hydrogen is particularly interesting in that it apparently represents the reverse of the Fischer–Tropsch process for methanol synthesis.

In summary we have demonstrated that photoexcitation of $\text{Fe}(\text{MeOH})$ in the violet leads primarily to metal insertion into the O–H bond whereas u.v. photolysis causes the activation of the C–O bond. Prolonged u.v. photolysis causes the dissociation of MeOFeH to CO, H_2 , and FeH_2 , and/or H_2 , and FeCO . The reactions and photochemistry of methanol with atomic and molecular iron in solid argon will be discussed in detail elsewhere.

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