Activation of Ethane, Propane, and Cyclopropane by Photoexcited Iron Atoms

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Monoatomic iron undergoes photoinsertion into the carbon–hydrogen bonds of ethane and n-propane and into the carbon–carbon bond of cyclopropane.

Previous studies in our laboratory have shown that the first row late transition metals, with the exception of nickel, will undergo photo-insertion into the carbon–hydrogen bonds of methane to yield CH_3MH.[1,2] Subsequently, Ozin and co-workers[3] were able to show the reversibility of the Fe/CH_4 reaction *via* wavelength selective narrow-band irradiation. Thus, irradiation into the 300 nm atomic line of Fe atoms in CH_4 produces the insertion product whereas irradiation into the 420 nm band of CH_3FeH yields CH_4 and Fe. No reaction between di-iron and methane was observed in these studies.[1,4] Here we report the reactions between iron atoms and ethane, n-propane, and cyclopropane compounds which, unlike methane, can experience both C–H and/or C–C bond activation.

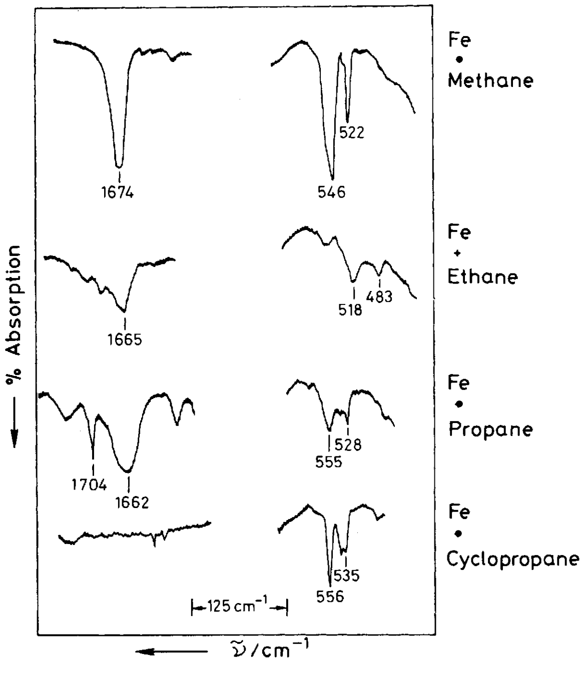

Figure 1. Infrared absorption spectra of the reaction products of iron atoms with methane, ethane, n-propane, and cyclopropane in solid argon. Each matrix was photolysed through a quartz window with a focused 100 W short arc mercury lamp during the deposition.

In each instance iron atoms were codeposited with a mixture of argon and the respective hydrocarbon on to a polished copper surface cooled to 10 K. The sample was irradiated with the u.v. light from a focused 100 W short arc mercury lamp. Infrared spectra were measured with a Beckman IR-9 spectrometer. The rates of deposition of the metal, alkane, and argon were measured with a quartz crystal microbalance. For the normal alkanes, new peaks developed in both the Fe–C and Fe–H stretching regions when the matrix was irradiated with u.v. light during the period of deposition. Peaks at 1674 and 522 cm^{-1} have been previously assigned to the Fe–H and Fe–C stretching modes, respectively, for the insertion product CH_3FeH.[1] Similar absorption bands in the Fe–H and Fe–C stretching regions were observed upon the cocondensation of iron atoms with either ethane or n-propane in solid argon as shown in Figure 1. The presence of these new absorptions suggests that photoinsertion of Fe atoms into the C–H bonds of ethane and n-propane has taken place yielding, in analogy with the Fe/CH_4 system, C_2H_5FeH and C_3H_7FeH, respectively.

Figure 2 shows the effect of changing the alkane–argon ratio on the spectra of the insertion products in the Fe–H stretching region. There is a red shift in the Fe–H stretching of RFeH (where R = CH_3, C_2H_5, C_3H_7) in going from the argon matrix to a neat matrix. In contrast to the Fe/CH_4 system[1] where the highest yield of CH_3FeH was obtained in a neat matrix, the yield of the insertion products from the higher alkanes did not change appreciably as the concentration of the alkane was increased. These observations possibly suggest that for the higher alkanes the quantum yield of RFeH (where R = C_2H_5, C_3H_7, ... *etc.*) will be even less sensitive to the concentration of the alkane in the matrix.

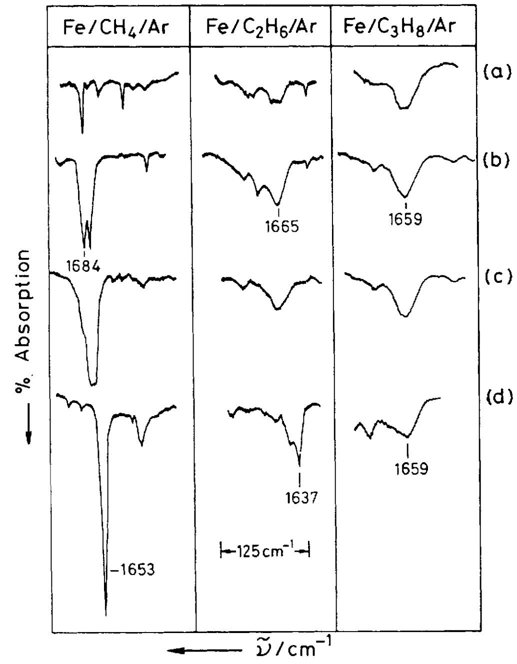

Figure 2. The H–Fe stretching region.

	Molar ratio		
	Fe : CH$_4$: Ar	Fe : C$_2$H$_6$: Ar	Fe : C$_3$H$_8$: Ar
(a)	2.7 : 10 : 1000	5.7 : 10 : 1000	5.0 : 40 : 1000
(b)	2.6 : 80 : 1000	5.7 : 29 : 1000	5.0 : 80 : 1000
(c)	5.2 : 660 : 1000	5.7 : 54 : 1000	3.7 : 54 : 1000
(d)	1.0 : 370 : 0	1.6 : 110 : 0	1.0 : 260 : 0

Two new peaks at 535 and 556 cm^{-1} were observed when iron atoms were codeposited with cyclopropane in solid argon with u.v. photolysis ($\lambda > 300$ nm). The absence of any absorption in the Fe–H stretching region (Figure 1) indicates that iron atoms have inserted into the carbon–carbon bonds of cyclopropane to form the metallacyclobutane. Surprisingly, iron atoms do not react with cyclopropane in a neat matrix, in contrast with the reaction of iron atoms with methane where the highest yield of insertion product was obtained in a neat matrix. This unexpected observation might result from the cyclopropane cage acting as a more efficient heat sink.

Di-iron, and possibly tri-iron, were also found to react with cyclopropane in solid argon. Wavelength selective broad-band irradiation of the matrices, as well as varying the molar concentrations of iron to argon, were the determining factors in discriminating between the mono-iron insertion product and the di- or tri-iron insertion products. These reactions will be discussed in detail in a future publication.

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