

Hydrocarbon Complexes of Iron Carbonyls Formed Photochemically in Argon Matrices at 17 K

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Irradiation of pentacarbonyliron with ethene in an argon matrix gives $(C_2H_4)Fe(CO)_4$, while ethyne reacts with the carbonyl under similar conditions to give a complex of 1-buten-3-yne.

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Matrix isolation coupled with absorption spectrometry has recently been shown to be a convenient method for the study of photochemical reactions of transition metal carbonyl derivatives (1). Products were detected which could not be prepared by standard thermal methods.

Further studies with ethene and normal and deuterated ethyne have now been carried out. A mixture of the hydrocarbon and pentacarbonyliron in an argon matrix (proportions $\sim 10:1:100$) at 17 K has been subjected to photolysis by radiation from a mercury lamp filtered to exclude wavelengths < 312 nm and between 417 and 676 nm.

Reaction of ethene with pentacarbonyliron during irradiation produces carbon monoxide and a monoalkene complex, $(C_2H_4)Fe(CO)_4$, a compound previously prepared by a high-pressure reaction (2).

A comparison of the important new bands in the vibrational spectrum (Perkin-Elmer 225, CsI optics), with the fundamental wave numbers previously reported appears in Table 1. Further irradiation leads to new bands, such as 1490 and 1218 cm^{-1} , which may indicate loss of further carbon monoxide from the alkene complex.

Reactions of ethyne with iron carbonyls yield complex mixtures of products under conventional conditions (3). In the present experiments, spectrometric changes during photolysis indicate production of 1-buten-3-yne, which complexes with the iron via the alkyne group only. The principal evidence for this comes from new bands for $C_2H_2(C_2D_2)$ at 1709 (1560), co-ordinated $C\equiv C$ vibration (4); 1547 (1462), uncoordinated $C=C$ (5); 912 (796), methylene wag of vinyl group (5); and 672 (531) cm^{-1} , CH bending vibration of $C\equiv CH$ group which is presumably no longer linear. Dimerization of ethyne to 1-buten-3-yne in the presence of copper(I) salts was discovered by Nieuwland *et al.* about 1930 (6), but the present work appears to have provided the first evidence for a complex of 1-buten-3-yne with a metal other than copper. Photolysis of ethyne itself, either gaseous or solid, requiring light of wavelength < 257 nm, produces 1-buten-3-yne as a minor by-product and then only under special conditions (7).

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TABLE 1. Comparison of wave numbers of $(C_2H_4)Fe(CO)_4$ in argon matrix and gas

Gas (2)	Ar matrix
3090	*
3024	*
2088	2090
2007	2009
1986	1992
1511	1508
1446	*
1200	1195
942	*
704	711
	635
	608

*Masked by remaining ethene.

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