Primary Photochemistry of Matrix Isolated Tricarbonylcyclobutadieneiron

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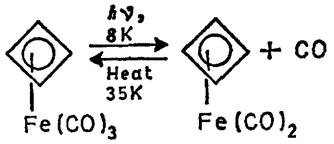
Summary The primary photochemical process in tricarbonylcyclobutadieneiron matrix isolated at 8 K is loss of carbon monoxide and formation of dicarbonylcyclobutadieneiron.

Irradiation of tricarbonylcyclobutadieneiron (I) in a perfluoropropane or a neopentane matrix at 77 K ($\lambda >$ 2200 Å) has been reported to give rise to cyclobutadiene and tricarbonyliron on the basis of an e.s.r. signal attributed to the tricarbonyliron.[1] Irradiation of (I) in solution in the presence of dienophiles gave rise to cyclobutadiene adducts[1]



(I) (II)

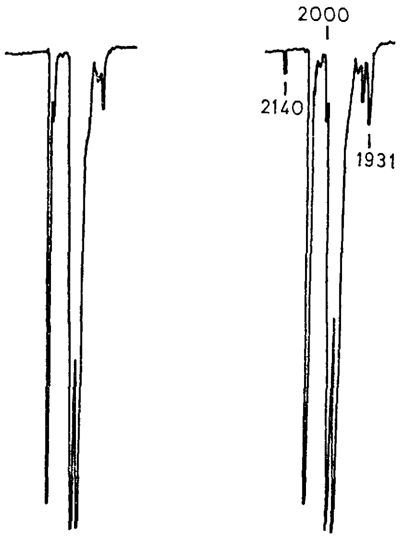


Figure. Carbonyl region of the i.r. spectrum of tricarbonylcyclobutadieneiron matrix isolated in argon at 8 K before irradiation (left) and after 10 min irradiation (right).

of the type originally observed by Pettit.[2] Pettit has pointed out, however, that in the irradiation of (I) it is possible that the primary photochemical process might be *loss of* carbon monoxide with subsequent formation of dicarbonylcyclobutadiene(dienophile)iron which then gives the cyclobutadiene adduct without generation of free cyclobutadiene.[3]

Recent interest in the spectroscopic investigation of cyclobutadiene[4] has led us to re-examine the photochemistry of (I). Irradiation (>2800 Å) of (I) matrix isolated (1 : 700) in krypton gave rise to new bands at 2140 (weak), 2000 (medium), and 1931 cm^{-1} (intense) (see Figure). These bands were shown to be due to primary photoproducts by plotting intensity *vs.* time. The band at 2140 cm^{-1} is assigned to carbon monoxide and the bands at 2000 and 1931 cm^{-1} to dicarbonylcyclobutadieneiron. Similar experiments in argon gave the same bands. The band assignments are corroborated by warming the argon matrix to 35 K which reverses the photochemical reaction. Continued irradiation destroys the primary products (II). Even prolonged irradiation of (I) in krypton or argon does not give cyclobutadiene or its photoproduct, acetylene. It is thus clear that Pettit's suggestion[3] concerning the primary photochemistry of tricarbonylcyclobutadieneiron is correct under our conditions. The reason for elimination of carbon monoxide in matrix photolysis and elimination of cyclobutadiene in vapour-phase photolysis[1] is not apparent.

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