Photoreactions of Pyridine- and 3-Bromopyridine-pentacarbonyltungsten in Argon Matrices at 12 K

By ANTONY J. REST* and JOHN R. SODEAU

(*Department of Chemistry, University of Southampton, Southampton* SO9 5NH)

Summary Infrared spectroscopy provides evidence that 366 nm photolysis of [$W(CO)_5L$], where L = pyridine or 3-bromopyridine, in an argon matrix at 12 K produces [$W(CO)_5$]; the reaction is shown to be photochromic by subsequent irradiation at 435 nm.

PHOTOCHEMICAL studies of [$W(CO)_5L$] (L = *N*-donor) in solution at room temperature have shown that the quantum yields (Φ) of reactions (1) and (2) are sensitive to wavelength. Short-wavelength irradiation causes more efficient loss of CO (Φ_{CO} = 0·002 at 436 and 0·04 at 254 nm; Φ_L = 0·63 at 436 and 0·34 at 254 nm, where L = pyridine).[1]

$$[W(CO)_5L] \xrightarrow{h\nu} [W(CO)_4L] + CO \qquad (1)$$

$$[W(CO)_5L] \xrightarrow{h\nu} [W(CO)_5] + L \qquad (2)$$

The photolysis of metal carbonyls in rare-gas matrices at low temperatures has provided much information concerning the structure of reactive species.[2] These are generally those proposed as intermediates in primary photochemical processes, which, in keeping with many room temperature experiments[3] involve the loss of CO as in reaction (1). We report an investigation into reactions (1) and (2) in which we provide evidence for the photolability of L in an argon matrix at 12 K.

Photolysis of a matrix mixture of [$W(CO)_5$(pyridine)] or [$W(CO)_5$(3-bromopyridine)] in argon at 12 K with a filtered medium-pressure Hg arc ($320 < \lambda < 390$ nm) produced, in both cases, new i.r. bands at 1962·5(s) and 1930·7(m) cm^{-1} [Figure A (i and ii)] due to a new species (I). No absorption was observed at 2138 cm^{-1}, the region associated with the production of CO in a matrix. When much of (I) had been formed, further bands appeared at

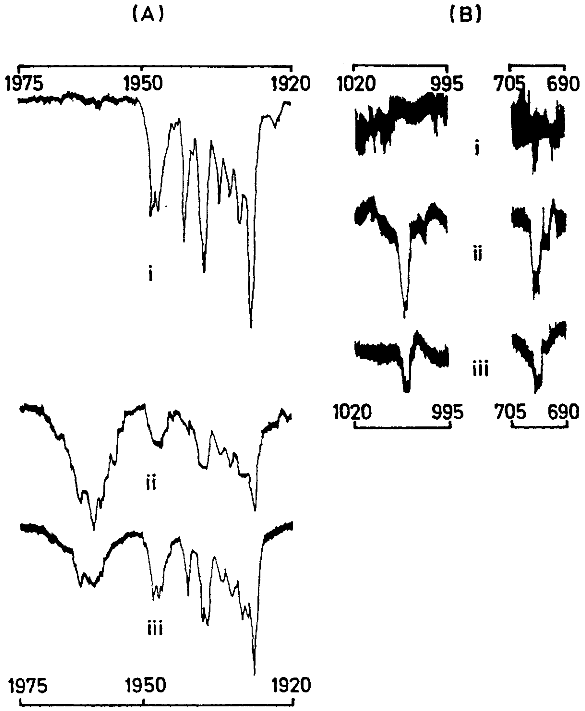

FIGURE. Infrared spectra from experiments with [$W(CO)_5$(3-bromopyridine)] co-condensed with argon at 12 K: (A) terminal CO stretching region (i) before photolysis, (ii) after photolysis at 366 nm for 30 min, and (iii) after photolysis at 435 nm for 50 min; (B) free ligand region in an experiment with twice as much sample on the window as in (A) and spectra recorded with 5 × signal expansion (i) before photolysis, (ii) after photolysis at 366 nm for 30 min, and (iii) after being left in the beam of a Grubb-Parsons Spectromajor spectrometer overnight.

1006·6 and 700·2 cm^{-1} [Figure B (i and ii)] in the case where L was 3-bromopyridine. These absorptions are consistent with the strongest absorptions in the i.r. spectrum in a separate experiment with 3-bromopyridine in argon (MR 1:2000) at 12 K. We identified (I) as [$W(CO)_5$] by comparison with the work of Turner *et al.*[4] on the photolysis of [$W(CO)_6$] in low temperature matrices.

Subsequent irradiation of the matrix at 435 nm, using a medium pressure Hg arc and a Bausch and Lomb high-intensity monochromator, caused a regeneration of the starting spectrum and a decrease in the bands produced in the first photolysis [Figure A(iii)]. Reversal was also observed if the sample was left for a long time in the beam of the i.r. spectrometer [Figure B(iii)].

Photolysis with an unfiltered medium-pressure Hg arc produced a complicated spectrum consisting of a band at 2138 cm^{-1} and absorptions associated with lower carbonyls. Free CO was also produced when the matrix was irradiated with a low-pressure Hg lamp ($>99\%$ $\lambda = 254$ nm).

The observation of free CO and L shows that both reactions (1) and (2) can take place in a matrix at 12 K, with process (2) being photochromic. The photodetachment of ligands with a high molecular weight has not been previously demonstrated.

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