Photoionisation of π-Cyclopentadienylnitrosylnickel in an Argon Matrix

By Oliver Crichton and Anthony J. Rest*

(*Department of Physical Chemistry, University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EP)

Summary I.r. spectroscopy provides evidence for the reversible production of an ion pair, $(\pi\text{-}C_5H_5)Ni^+NO^-$, by photolysis of $(\pi\text{-}C_5H_5)NiNO$ in an argon matrix at 20 K.

Various unstable species have been produced by the photolysis of matrix isolated precursors.[1] Generally, neutral products are formed by homolytic cleavage of bonds giving rise to pairs of radicals, or by the ejection of a stable fragment. Ions have only been produced from matrix isolated substrates by electron transfer during photolysis of co-isolated alkali metal atoms,[2] or by electron bombardment.[3] We report an unusual example of ion formation during photolysis of a neutral compound.

The spectrum of $(\pi\text{-}C_5H_5)NiNO$ in an argon matrix (dilution 1 : 2000—1 : 10,000) shows a strong terminal nitrosyl band (1838, 1834, and 1829 cm^{-1}) and various weaker bands, the strongest of which are assignable to C–H deformations of the hydrocarbon moiety (1011 and 806 cm^{-1}). All bands appear as multiplets owing to matrix splitting effects.[1] Photolysis with a filtered medium pressure Hg arc ($230 < \lambda < 280$ nm; 30 min) caused a considerable reduction in the intensity of the nitrosyl band, and the production of a strong new band (1390 cm^{-1}). Weaker bands were also observed at 1007 and 797 cm^{-1}. The strong band at 1390 cm^{-1} shifted by 24 cm^{-1} to 1366 cm^{-1} when $(\pi\text{-}C_5H_5)Ni^{15}NO$ was photolysed under similar conditions. Irradiation using a different filter ($290 < \lambda < 350$ nm; 10 min) caused almost complete regeneration of the original spectrum. The formation of the product species was almost completely reversible even after several hours of forward photolysis. No reversal was observed on warming the matrix to 30 K and recooling to 20 K.

It is difficult to account for the 1390 cm^{-1} band as a co-ordinated nitrosyl vibration, either terminal or bridging, as it lies completely outside the wavenumber range for both linear and bent terminal nitrosyls (1850—1625 cm^{-1}) and nitrosyl bridged species are excluded by the high dilution. This band is, however, close to the reported range of NO^- vibrations (1375—1350 cm^{-1})[2] and has been assigned on this basis because of the ^{15}N isotope shift. The similarity of the product hydrocarbon spectrum to that of the parent species is consistent with a $(\pi\text{-}C_5H_5)Ni$ fragment. It is thus probable that an ion pair $(\pi\text{-}C_5H_5)Ni^+NO^-$ has been generated by photolysis. The ease of photochemical reversibility of its formation, even after prolonged photolysis, suggests a fairly close ion pair so that the lack of thermal reversibility probably reflects a genuine, if small, activation energy barrier to recombination.

We thank the S.R.C. and I.C.I. for a C.A.P.S. Studentship to O.C. and the Royal Society for a Pickering Research Fellowship to A.J.R.

(*Received, 25th April* 1973; *Com.* 575.)

---

[1] J. S. Ogden and J. J. Turner, *Chem. in Britain*, 1971, **7**, 186.

[2] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, 1971, **55**, 3404.

[3] D. E. Milligan, M. E. Jacox, and W. A. Guillory, *J. Chem. Phys.*, 1970, **52**, 3864.