Journal of Organometallic Chemistry, 266 (1984) C27—C30
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE REVERSIBLE DECARBONYLATION OF METHYL- AND ACETYLDICARBONYL(η^5-CYCLOPENTADIENYL)IRON COMPLEXES IN POLYVINYL-CHLORIDE FILM MATRICES AT 12—200 K

RICHARD H. HOOKER, ANTONY J. REST* and IAN WHITWELL
Department of Chemistry, The University, Southampton S09 5NH (Great Britain)

(Received January 27th, 1984)

Summary

Infrared spectroscopic experiments using polyvinyl chloride film matrices at 12—200 K have shown for the first time that the photoinduced decarbonylation of $Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)$ is thermally reversible, and that the photolysis of $Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)$ leads to the reversible formation of the new species $Fe(\eta^5\text{-}C_5H_5)(CO)(CH_3)$.

The photochemical decarbonylation of $Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)$ (I) in solution has been shown [1], using ^{13}CO labelling, to proceed via loss of a terminal CO group (Scheme 1). In the presence of PPh_3 the reaction product was

$$\begin{tikzcd} \underset{(I)}{Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)} \arrow[r, "h\nu"] & \underset{(II)}{Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)} + CO \arrow[d] \\ & \underset{(III)}{Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)} \end{tikzcd}$$

SCHEME 1

$Fe(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(COCH_3)$ (IV) [1], which may be taken to indicate that the reaction of the proposed intermediate, II, with added PPh_3 is more facile than methyl migration to give III. An alternative pathway would be for III, once formed, to undergo an insertion reaction to give IV. Another reactive species, $Fe(\eta^5\text{-}C_5H_5)(CO)(CH_3)$ (V), is thought [2,3] to be involved in the photosubstitution reactors of III with phosphine donors (L) which lead to $Fe(\eta^5\text{-}C_5H_5)(CO)(L)(CH_3)$ complexes.

0022-328X/84/$03.00

Recently, II has been observed [4,5] directly on photolysis of I in a variety of frozen gas matrices at 12 K. Attempts to generate V on photolysis of III in similar matrices [4] and also in solid paraffin matrices [3] have been unsuccessful, however the Ru analogue of V has been observed under these conditions [3,6]. We report here on the photolysis of I and III and the subsequent thermal reactions observed in PVC films at 12—200 K.

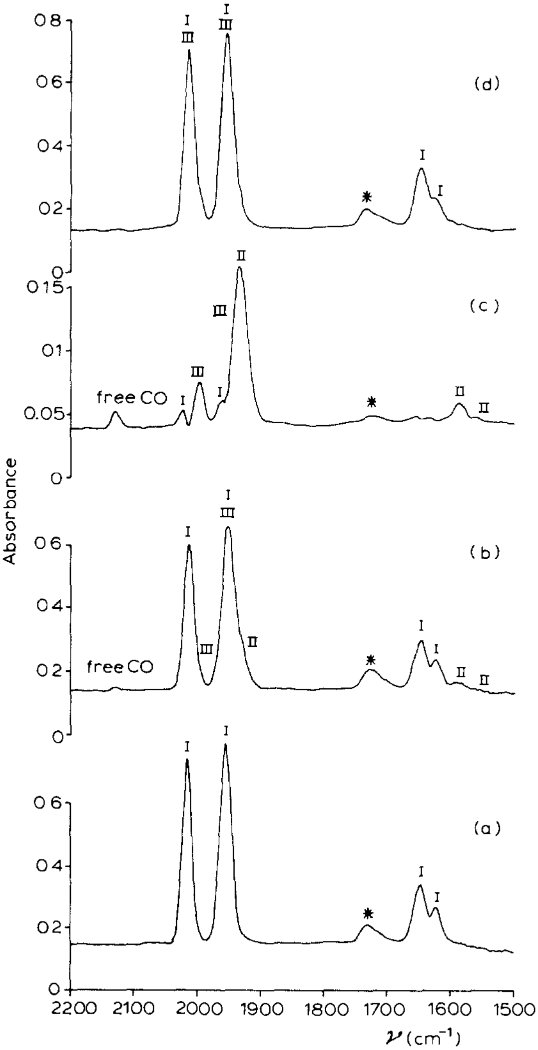

Fig. 1. IR spectra (Nicolet 7199 FTIR spectrometer; 1 cm^{-1} resolution) from an experiment with Fe(η^5-C_5H_5)$(CO)_2(COCH_3)$ (I) in a PVC film matrix at 12 K: (a) before irradiation, (b) after 30 min irradiation ($300 < \lambda < 370$ nm), (c) difference spectrum, i.e. (b) − A(a), where A is a scaling factor, and (d) after warming the matrix to 200 K. The bands marked II and III are for Fe(η^5-C_5H_5)(CO)$(COCH_3)$ and Fe(η^5-C_5H_5)$(CO)_2(CH_3)$, respectively and that marked (*) is due to ketone groups in the PVC matrix.

Figure 1(a) shows the IR spectrum of I in a PVC film* matrix at 12 K. Two terminal CO stretching bands at 2016 and 1956 cm^{-1} are seen as well as two acetyl CO bands at 1649 and 1626 cm^{-1}, where the latter have been attributed [4,5] to conformational isomers of I. Irradiation of the film (Fig. 1(b) and 1(c)) led to the formation of II, free CO and III by analogy with the photoreaction data for I in a frozen gas matrix (Table 1). The formation of II from I at 12 K is not photochemically reversible [4]. Extended visible irradiation ($\lambda > 400$ nm) results in complete conversion of II to III. However, on slowly warming the film to ca. 200 K (Fig. 1(d)) the IR bands for I were found to increase in intensity together with those for III whilst the bands for II and for free CO disappeared. This indicates that II can react thermally with CO to regenerate I, cf. the formation of IV from reaction of II with PPh_3 in solution, as well as undergo a methyl migration. The possibility that the latter process occurs preferentially from one conformer [5] of II is at present being investigated.

Irradiation ($300 < \lambda < 370$ nm) of an authentic sample of III in a similar PVC film at 12 K produced free CO and a single new band (ν(CO) 1951 cm^{-1}) in the terminal CO stretching region. This reaction was reversed completely on warming the film to ca. 40 K and we identify the photoproduct as being the 16-electron fragment $Fe(\eta^5\text{-}C_5H_5)(CO)(CH_3)$ (V), cf. $Ru(\eta^5\text{-}C_5H_5)(CO)(CH_3)$ (Table 1). The facile thermal reversal of the decarbonylation of III in the film at temperatures $\leqslant$ 40 K would explain why V has not been observed in solid paraffin matrices [3] at 40—77 K. It is probable that the failure to photogenerate V from III in frozen gas matrices, even under vigorous irradiation conditions [4], is due to a rapid back reaction of the photogenerated fragments in the closely confined gas matrix environment. In contrast, the polymer film matrices are thought to provide a more cavernous medium [8] in which the "cage effect" is a less serious problem.

TABLE 1

INFRARED BAND POSITIONS (cm^{-1}) OF $Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)$, $Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)$ AND $Ru(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)$ AND THEIR PHOTOPRODUCTS IN PVC FILMS AND CH_4 MATRICES AT 12 K

Complex	PVC	CH_4 [a]
$Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)$	2016	2021.0
	1956	1961.2
	1649	1663.8
	1626	1630.7
$Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)$	1934	1947.5
	1587	1602.0
	1562	1564.7
$Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)$	2001	2012.2
	1942	1956.4
$Fe(\eta^5\text{-}C_5H_5)(CO)(CH_3)$	1951	—
$Ru(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)$	2011	2018.4
	1945	1958.3
$Ru(\eta^5\text{-}C_5H_5)(CO)(CH_3)$	1925	1943.4

[a] Mean band positions are given in cases where matrix splitting was observed [4—6].

---

*The film was cast from 1,2-dichloroethane solution. Details of the solvent casting technique, the purity of reagents and the stringent precautions taken are given in ref. 7.

The above results illustrate the advantages of polymer film matrices over frozen gas matrices for studying the thermal reactivity of low temperature photoproducts over a wide temperature range and also the complementarity of polymer film and gas matrix techniques. For example, using polymer film matrices, it is possible to trap in these matrices, at cryogenic temperatures, reactive species which cannot be formed by similar "in situ" photolysis of molecules in conventional frozen gas matrices. Specifically, we have been able to observe the reversible decarbonylation of I and III not seen previously and have thereby provided firmer foundations for the mechanisms of insertion and decarbonylation reactions [9] which invoke the principle of microscopic reversibility.

We thank the SERC for a Research Studentship (to RHH) and for support (to AJR) and the British Gas Corporation for a Scholarship (to IW).

References

1 J.J. Alexander, J. Am. Chem. Soc., 97 (1975) 1729.
2 C.R. Folkes and A.J. Rest, J. Organomet. Chem., 136 (1977) 355.
3 R.J. Kazlauskas and M.S. Wrighton, Organometallics, 1 (1982) 602.
4 D.J. Fettes, R; Narayanaswamy and A.J. Rest, J. Chem. Soc. Dalton Trans., (1981) 2311.
5 R.B. Hitam, R. Narayanaswamy and A.J. Rest, J. Chem. Soc. Dalton Trans., 1983, 615.
6 H.G. Alt, K.A. Mahmoud and A.J. Rest, J. Chem. Soc. Dalton Trans., (1984) in press.
7 R.H. Hooker and A.J. Rest, J. Chem. Soc. Dalton Trans., (1984) in press.
8 J.K. Burdett, Coord. Chem. Rev., 17 (1978) 1.
9 A. Wojcicki, Adv. Organomet. Chem., 11 (1973) 87; 12 (1974) 32.