

Preliminary communication

Infrared evidence for the formation of acetyl- and methyltetracarbonyl-manganese on photolysis of acetyl- and methylpentacarbonylmanganese in matrices at 15°K

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Kinetic studies of organometallic reactions have enabled mechanisms to be proposed¹. These mechanisms would be put on a firmer basis if the species postulated as intermediates could be shown to exist and if reactions could be observed directly and in isolation. As part of a general investigation of species which could be intermediates in organometallic reactions by low temperature techniques, I report the isolation and reactivity of species produced from $\text{CH}_3\text{COMn}(\text{CO})_5$ and $\text{CH}_3\text{Mn}(\text{CO})_5$.

Photolysis (5 min; $300 < \lambda < 360$ nm) of a matrix mixture of $\text{CH}_3\text{COMn}(\text{CO})_5$ (I) and argon (approx. 1/600) at 15°K produced new infrared bands at 1613, 1957, 1993, 2006, 2014, 2087 and 2113 cm^{-1} associated with metal carbonyl species (II, III) and a band at 2138 cm^{-1} which corresponds to CO. Further photolysis with the same radiation caused increases in all the new bands but photolysis with a different filter (5 min; $\lambda > 320$ nm) caused bands associated with the small amount of I which remained and those at 1613, 1957, 2006 and 2087 cm^{-1} to disappear while those at 1993, 2014, 2113 and 2138 cm^{-1} continued to grow. Separate experiments (see below) showed that the bands at 1993, 2014 and 2113 cm^{-1} were due to $\text{CH}_3\text{Mn}(\text{CO})_5$ (III).

Photolysis (10 min; $230 < \lambda < 280$ nm) of a matrix mixture of $\text{CH}_3\text{Mn}(\text{CO})_5$ (III) and argon (approx. 1/600) at 15°K produced new infrared bands at 1956, 2002, 2092 and 2138 cm^{-1} associated with a metal carbonyl species (IV) and CO. Further photolysis (5 min; $\lambda > 280$ nm) caused quantitative reversal of IV and CO to III.

The infrared spectrum of IV showed terminal C—O stretching bands ($\nu(\text{C—O})$: 1956 s, 2002 s, 2092 w cm^{-1}) consistent with a trigonal bipyramidal (C_{3v}) molecule $\text{CH}_3\text{Mn}(\text{CO})_3\text{CO}$. The weak band at 1613 cm^{-1} in the infrared spectrum of II, which may be assigned to a ketonic C—O stretching vibration, and the similarity of the terminal C—O band pattern of II ($\nu(\text{C—O})$: 1957 s, 2006 s, 2087 w cm^{-1}) and IV suggest that II has a trigonal bipyramidal structure $\text{CH}_3\text{COMn}(\text{CO})_3\text{CO}$. Infrared bands associated with I–IV were observed in other spectral regions but these were considerably weaker making assignment difficult. These results, the results from analogous studies of $\text{CF}_3\text{COMn}(\text{CO})_5$ and $\text{CF}_3\text{Mn}(\text{CO})_5$ and the results of labelling with ^{13}C CO in the complexes and by doping the matrix will be reported elsewhere².

Attempts to reverse steps I \rightarrow II and II \rightarrow III by photolysing with a different source or by raising the temperature of the matrix for several minutes were unsuccessful.

Step III \rightarrow IV was reversed quantitatively by irradiating with $\lambda > 280$ nm and some reversal was produced by raising the temperature of the matrix to 30°K for 5 minutes. The isolation of II and IV and their thermal stability up to 30°K shows that steps II \rightarrow I, II \rightarrow III, III \rightarrow II, and IV \rightarrow III have activation energy requirements. The partial recombination of IV and CO at 30°K indicates that the activation energy for this step is less than for the other steps.

Photolysis of I and III in CO matrices at 15°K demonstrated that steps I \rightarrow II and II \rightarrow III were equally as facile in CO as in argon, but step III \rightarrow IV was partially inhibited. The inhibiting of step III \rightarrow IV probably arises because photolysis produces IV* with sufficient excess energy to overcome the activation energy barrier for IV \rightarrow III. If IV* is surrounded by a cage of CO molecules there is a greater chance of recombination than if there are at most two CO molecules in the same cage, as with the argon experiments. The similar ease of steps I \rightarrow II and II \rightarrow III in CO and argon arises because the sequence I \rightarrow II \rightarrow III has the production of two stable molecules as its driving force and this is favoured by the photolysis conditions and the UV/visible spectra of the species. The sequence I \rightarrow II \rightarrow III indicates that the first step in the decarbonylation of $\text{CH}_3\text{COMn}(\text{CO})_5$, which solution infrared kinetic studies indicate is a dissociative process involving methyl migration³, is loss of CO probably from the equatorial position.

The results described above are somewhat different from those described by Ogilvie⁴ at the same time as this study was nearing completion. He claimed that photochemical means could be used to effect partial conversion of a methylmanganese carbonyl species to an acetylmanganese carbonyl species. Several points are worth noting:

(i) In order to "see" new bands in the C—H deformation, Mn—C—O deformation and Mn—C stretching regions⁴, a considerable thickness of sample has to be deposited on the sample window. Under these circumstances the poor thermal conductivity of solid argon may mean that two or more metal carbonyl molecules may be placed in the same cage in the outer layers of the matrix sample. The essential feature of meaningful matrix isolation experiments, which is the isolation of single molecules well separated from each other by inert matrix, will thus be lost.

(ii) The proposed⁴ ketonic C—O vibration in $\text{CH}_3\text{COMn}(\text{CO})_x$ at 1767 cm^{-1} is at a high position for this kind of vibration and may well be due, as a consequence of the thickness

of the film, to a bridging $\text{Mn}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Mn}$ vibration. Alternatively, as experiments in this laboratory have shown, the use of an unfiltered Hg arc lamp of the type described⁴ for long photolyses of metal carbonyls produces extensive decomposition to $\text{M}(\text{CO})_x(\text{L})_y$ ($x = 1-3$, $y = 0, 1$) species⁵ which have terminal C—O stretching vibrations in the range $1700-1900\text{ cm}^{-1}$.

(iii) No attempt was made by Ogilvie⁴ to rationalise the terminal C—O stretching frequency region of the spectra he described. This region, most of all for metal carbonyl species, gives good structural information and, moreover, because of the high intensity of the bands, it is possible to detect small amounts of transient species in sequences in this region.

(iv) The experiments described in this communication take account of all the bands produced in thin film high dilution samples and no evidence for the conversion of methylmanganese carbonyl to acetylmanganese carbonyl could be found.

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