Photochemical Production of Acetylmanganese Carbonyls in an Argon Matrix at 17K

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Summary. Vibrational spectrometric data indicate that absorption of light in electronic transitions of methylmanganese and trifluoromethylmanganese pentacarbonyls in argon matrices at 17K leads to formation of the corresponding acetylmanganese carbonyl compounds having fewer than five terminal carbonyl groups.

IN the course of an investigation of the vibrational spectra of small hydrocarbon radicals,[1] a suitable parent material was sought from which the methyl radical might be derived by simple processes. One compound considered was methylmanganese pentacarbonyl, which strongly absorbs u.v. radiation in a region convenient because of the availability of intense photolytic sources.

Preliminary experiments in 1966 were conducted in the Cambridge Department of Physical Chemistry on a Unicam SP100 spectrophotometer,[1] and a model AC3L-110 Cryotip refrigerator (Air Products) which was provided by a Royal Society grant. Further experiments in Newfoundland involved a Perkin-Elmer model 225 spectrophotometer and a model AC2L-110 Cryotip refrigerator. In all experiments, argon was used as inert diluent, and the temperature, 17K, was sufficiently low for diffusion processes in the solid to be severely inhibited. Matrix experiments with other metal carbonyls indicate satisfactory matrix rigidity. Measurements of electronic and vibration–rotational spectra of vapours and of vibrational spectra in solution, near ambient temperatures, were performed on various calibrated instruments.

When samples of $XMn(CO)_5$, in which $X = CH_3$, CD_3 or CF_3, at molar ratios from 1 : 150 to 1 : 300 of argon at 17K, are subjected to irradiation by means of HPK125 Hg (125w), 93107 Cd (25w), or 93146 Hg + Cd + Zn (90w) lamps (Philips), the vibrational absorptions of the parent compound decrease in intensity, and new absorptions appear. Measured between 370 and 4500 cm^{-1}, the new bands can be conveniently classified according to ranges with boundaries at 530, 700, 1900, and 2400 cm^{-1}. For all substances, no new absorptions are observed at wavenumbers exceeding 2400 cm^{-1}. A band at 2139 cm^{-1} is always due to carbon monoxide, as confirmed by the appropriately weaker band at 2092 cm^{-1} due to carbon-13 monoxide in natural abundance when duration of photolysis is sufficiently protracted. Transition-metal carbonyl compounds are known to detach carbon monoxide under photolytic conditions.[2] Many new bands of varying behaviour according to radiation source and photolysis duration appear between 1900 and 2108 cm^{-1}; these presumably belong to various metal carbonyl compounds derived from the parent materials after loss of carbon monoxide. The great intensity (and abundance) of the latter absorptions compared with bands in other regions makes difficult the correlation of various sets of absorptions to particular species. Features appearing between 530 and 700 cm^{-1} are attributed to Mn–C–O deformation vibrations of new carbonyl derivatives as mentioned above. A narrow feature after $H_3CMn(CO)_5$ photolysis near 612 cm^{-1} is unlikely to signify methyl radicals[3] as there is no corresponding absorption at 450 cm^{-1} after $D_3CMn(CO)_5$ photolysis. New absorptions at 432 and 479 cm^{-1} obtained from parent materials in which $X =$ both CH_3 and CD_3, and similar wavenumbers for $X = CF_3$, are attributed to Mn–C valence-stretching vibrations in which the carbon atoms are in carbonyls. All these new absorptions are expected (qualitatively) on the basis of the known vibrational spectra of the parent compounds and other transition-metal carbonyl derivatives.[4]

For $X = CH_3$ or CD_3, no new absorptions were detected between 700 and 1900 cm^{-1} except after long irradiations with the powerful HPK125 lamp. Then, new weak absorptions appeared at 1767 and 1405 cm^{-1} ($X = CH_3$), and 1763 and 1073 cm^{-1} ($X = CD_3$). These absorptions are assigned to acetyl derivatives of manganese carbonyl species. The 1767 or 1763 cm^{-1} wavenumber is appropriate to the ketonic carbonyl group, and is different from 1844 or 1836 cm^{-1} of the acetyl radical;[5] the significant shift on deuteriation strongly indicates close proximity of hydrogen or deuterium atoms, so that a carbonyl group bridging two manganese atoms is excluded. The wavenumbers of ketonic carbonyl modes are 1673 cm^{-1} for $H_3CCOMn(CO)_5$ vapour and 1671 cm^{-1} in heptane solution.[6] The large discrepancy affords proof that the 1767 and 1763 cm^{-1} bands do not belong to acetylmanganese pentacarbonyls somehow formed from methylmanganese pentacarbonyls and carbon monoxide molecule photo-detached from another parent molecule nearby in the solid argon. The 1405 and 1073 cm^{-1} absorptions are attributed to deformation modes of the methyl groups, CH_3 and CD_3, respectively.

When $F_3CMn(CO)_5$ is photolysed as described above, a doublet appears at 1680—1690 cm^{-1}, appropriate to a ketonic carbonyl group. A band at 1335 cm^{-1} increases in intensity during photolysis at a rate parallel to the 1680 cm^{-1} doublet, whereas other bands between 950 and 1350 cm^{-1} grow at different rates. Other groups of bands are found near 450 and 600 cm^{-1} of which growth rates are not yet determined. $F_3CCOMn(CO)_5$ vapour has bands due to the trifluoroacetyl group at 1673 (carbonyl, 1663 in CCl_4 solution), 1141, 1192, and 1252 cm^{-1} (C–F valence-stretching). Thus, by analogy a trifluoroacetylmanganese carbonyl compound is deduced to be formed.

The number of terminal carbonyl groups in the new acetyl compounds is probably four, simply on the basis of mass conservation under the assumption of a rigid matrix. However, further loss of terminal carbonyls from these products would be possible under the prevailing photolytic conditions.

In all cases, absorptions attributed to the acetyl compounds increase during irradiation at a rate characteristic of not only a formation process, but also a concurrent photodecomposition. That the continued exposure to u.v. light seems readily to decompose these acetyl compounds is understandable, as in each case the known $XCOMn(CO)_5$ compounds, in which $X = CH_3$, CD_3, or CF_3, have a continuous electronic absorption about 30,000 cm^{-1}, where there is most intense emission from the Hg lamp. These are bands additional to the continuous absorptions of the corresponding $XMn(CO)_5$ compounds at greater wavenumbers, and further electronic absorption bands of the new acetyl compounds may also participate in photodecomposition processes.

An important difference between $XMn(CO)_5$ in which $X = CH_3$, *or* CF_3, is that the former compound can be fairly reversibly transformed to the acetyl compound,[7] whereas to convert $F_3CMn(CO)_5$ into $F_3CCOMn(CO)_5$ has not yet proved possible. The present experiments indicate that by photochemical means the partial conversion of a trifluoromethylmanganese species into a trifluoroacetylmanganese species can be effected.

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