Evidence for the Production of Hydridotetracarbonylmanganese, $HMn(CO)_4$, on *Reversible* Photolysis of Hydridopentacarbonylmanganese, $HMn(CO)_5$, in Argon at 15°K

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Summary Infrared evidence suggests that CO loss follows Cd line (2288 Å) photolysis of $HMn(CO)_5$ in argon at 15°K and that the photolysis can be *reversed* by use of $\lambda >$ 2850 Å

STUDIES by flash photolysis,[1] electron impact,[2] thermal decomposition,[3] and solution photolysis[4] have suggested that the primary step in transition-metal carbonyl reactions is dissociation. The matrix isolation technique[5] is well suited to a spectroscopic investigation of intermediates, particularly those produced photolytically. By using i.r. spectroscopy Sheline and his co-workers[6] and Massey and Orgel[7] have observed the u.v. photolysis of $M(CO)_6$ (M = Cr, Mo, or W) and $Fe(CO)_5$ in hydrocarbon matrices at 77°K and deduced that CO loss occurs. We present here preliminary results of an investigation of carbonyl fragments at 15°K.

The i.r spectra in the Figure show the result of photolysing a matrix mixture of $HMn(CO)_5$ in argon with different photolytic sources. The most striking features of these spectra are:

(i) in addition to CO, there are at least *two* photolytic products, depending on the photolytic system—a product (A) associated with the i.r. bands (1), (2) and (3) (in spectra (b) and (d) at 1970, 2001, and 2094 cm.$^{-1}$ respectively), which increase or decrease in intensity in the same proportions, and products (B) associated with bands (4), (5), (6), and (7) [spectrum (e)];

(ii) the quantity of CO produced is approximately consistent with the loss of one CO per $HMn(CO)_5$ in step (a) $\rightarrow$ (b) and further CO in step (d) $\rightarrow$ (e);

(iii) the production of (A) can be *reversed* [spectrum (c)], but since the radiation which promotes the reverse reaction also promotes some production of (B) it was not possible to convincingly demonstrate uptake of CO in step (b) $\rightarrow$ (c); and

(iv) even in experiments which produced 85% absorption due to (A), there was no evidence for H transfer[8] (analogous to CH_3 transfer) to give $HCOMn(CO)_4$, which would show a ketonic CO band in the 1600—1700 cm.$^{-1}$ region. The Mn–H vibration of the parent molecule is very weak and no change could be detected on photolysis.

$HMn(CO)_5$ and PF_3 react in the gas phase under u.v. irradiation (1000 w, high-pressure Hg arc) to give $HMn(CO)_x(PF_3)_{5-x}$.[9] This, together with the observations of

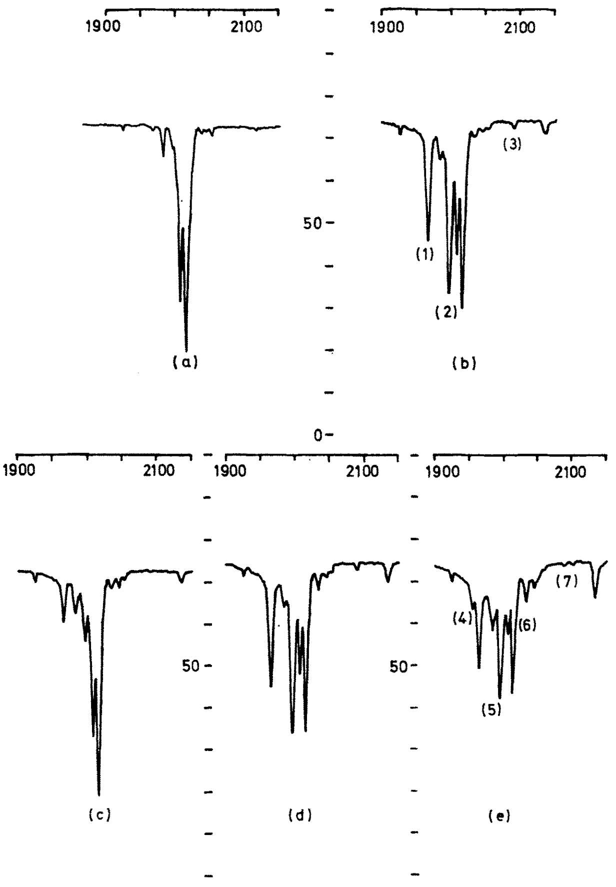

FIGURE. *I.r. spectra from a single* $HMn(CO)_5$ *photolysis experiment*: (a) *after* 30 *min. spray-on of* $HMn(CO)_5$ *in argon* (1 : 180) *at* 15°K; (b) *after* 20 *min. photolysis with* Cd-*line source* (2288 Å); (c) *after* 20 *min. photolysis with* Pyrex-filtered *medium pressure mercury arc* (i.e. *no radiation with* $\lambda <$ 2850 Å); (d) *after* 20 *min. photolysis with* Cd-*line source*; (e) *after* 20 *min. photolysis with* unfiltered *mercury arc. The same spectrum can be obtained by unfiltered mercury arc photolysis of* (a).

Sheline and Orgel, confirms that the most likely primary photolytic step is loss of CO. The i.r. spectra (b) and (d) are consistent with the production of a trigonal bipyramidal† (C_{3v}) molecule $HMn(CO)_3CO$, bands (1), (2) and (3) being the E and $2A_1$ CO stretching vibrations analogous to the three bands observed in $HCo(CO)_4$.[10] Thus loss of CO (probably equatorial[11]) is rapidly followed by slight rearrangement.[12] Spectrum (e) is not readily assigned but in addition to $HMn(CO)_4$ is probably due to $HMn(CO)_3$.

The primary photolytic products, CO and $HMn(CO)_4$, are in the same matrix cage and since they do not react in the absence of u.v. irradiation the activation energy for such a reaction must be sufficiently large to prevent any recombination at 15°K. However irradiation with $\lambda > 2850$ Å promotes the reverse reaction. This cannot be due to excitation of CO since this molecule has no absorption spectrum above 2100 Å. Presumably excitation of $HMn(CO)_4$ allows subsequent reaction with CO, while the photolysis of the parent molecule is largely suppressed.

The efficiency of the unfiltered medium-pressure mercury arc in producing both (A) and (B) is due to the high intensity of several lines in the mercury spectrum below 2850 Å, which strips first one then subsequent CO's faster than the radiation of $\lambda > 2850$ Å promotes recombination.

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† The i.r. spectra are less easily interpreted on the basis of a square pyramidal structure.

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