# The Metal–Metal Bond Dissociation Energy in Manganese Carbonyl

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THE radical, $\cdot Mn(CO)_5$, has been produced by the pyrolysis of manganese carbonyl vapour in a graphite effusion cell adjacent to the ion source in a mass spectrometer. The geometry of this assembly is similar to that described elsewhere.[1] At cell temperatures in the range 210—310° c, $Mn(CO)_5^+$ was observed at electron-impact energies below the appearance potential of $Mn(CO)_5^+$ from manganese carbonyl. This evidence for the production of the $\cdot Mn(CO)_5$ radical is further supported by the observation that with increasing cell temperatures the ratios $Mn_2(CO)_9^+/Mn_2(CO)_{10}^+$ and $Mn_2(CO)_8^+/Mn_2(CO)_{10}^+$ remained constant whereas the ratios $Mn(CO)_5^+/Mn_2(CO)_{10}^+$ and $Mn(CO)_4^+/Mn(CO)_{10}^+$ increased.

The ionization potential of $\cdot Mn(CO)_5$ (1) and the appearance potential of $Mn(CO)_5^+$ from manganese carbonyl (2) were measured relative to xenon using Warren's method.[2] The values obtained are I.P. = 8·44 ± 0·03 ev and A.P. = 9·26 ± 0·03 ev, respectively.

$$\cdot Mn(CO)_5 + e \rightarrow Mn(CO)_5^+ + 2e \quad (1)$$

$$Mn_2(CO)_{10} + e \rightarrow Mn(CO)_5^+ + \cdot Mn(CO)_5 + 2e \quad (2)$$

If one assumes that ions produced in (1) and (2) are energetically the same then the algebraic difference between (2) and (1) is the dissociation,

$$Mn_2(CO)_{10} \rightarrow 2 \cdot Mn(CO)_5 \quad (3)$$

for which $D$(Mn–Mn) = A.P. − I.P. = 18·9 ± 1·4 kcal. This low value for $D$ is in accord with the very long Mn–Mn bond length[3] of 2·93 Å and is to be compared with a previously reported value of 34 ± 13 kcal.[4]

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