

The Metal-Metal Bond Dissociation Energy in Manganese Carbonyl

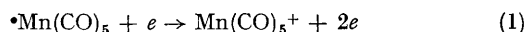
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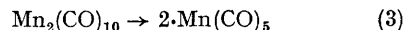
THE radical, $\bullet\text{Mn}(\text{CO})_5$, has been produced by the pyrolysis of manganese carbonyl vapour in a graphite effusion cell adjacent to the ion source in a mass spectrometer. The geometry of this assembly is similar to that described elsewhere.¹ At cell temperatures in the range 210–310° c, $\text{Mn}(\text{CO})_5^+$ was observed at electron-impact energies below the appearance potential of $\text{Mn}(\text{CO})_5^+$ from manganese carbonyl. This evidence for the production of the $\bullet\text{Mn}(\text{CO})_5$ radical is further supported by the observation that with increasing cell temperatures the ratios $\text{Mn}_2(\text{CO})_9^+/\text{Mn}_2(\text{CO})_{10}^+$ and $\text{Mn}_2(\text{CO})_8^+/\text{Mn}_2(\text{CO})_{10}^+$ remained constant whereas the ratios $\text{Mn}(\text{CO})_5^+/\text{Mn}_2(\text{CO})_{10}^+$ and $\text{Mn}(\text{CO})_4^+/\text{Mn}(\text{CO})_{10}^+$ increased.

The ionization potential of $\bullet\text{Mn}(\text{CO})_5$ (1) and the appearance potential of $\text{Mn}(\text{CO})_5^+$ 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.



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,



for which $D(\text{Mn-Mn}) = \text{A.P.} - \text{I.P.} = 18.9 \pm 1.4$ kcal. This low value for D is in accord with the very long Mn-Mn bond length³ of 2.93 Å and is to be compared with a previously reported value of 34 ± 13 kcal.⁴

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¹ D. R. Bidinosti and R. F. Porter, *J. Amer. Chem. Soc.*, 1961, **83**, 3737.

² J. W. Warren, *Nature*, 1950, **165**, 810.

³ L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 1957, **26**, 1750.

⁴ F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 1960, 533.