110. *The Heat of Sublimation and the Metal–Metal Bond Energy in* $Mn_2(CO)_{10}$.

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The heat of sublimation of $Mn_2(CO)_{10}$ has been estimated from measurements of the temperature-dependence of the equilibrium vapour pressure over the solid in the range 102—146° c. The result, 15·0 ± 0·5 kcal./mole, has been used with other thermochemical data and spectroscopically derived valency-state promotion energies to estimate the strength of the Mn–Mn bond. The result is 34 ± 13 kcal./mole.

UNTIL fairly recently there was no direct and unequivocal evidence for the existence of stable bonds between pairs of transition-metal atoms in chemical compounds. Within the past several years, however, the existence of such bonds has been recognized for several compounds. Infrared studies have suggested their existence in solid salts of $[Co^{II}(CN)_5]_2^{6-}$,[1] $[Ni^{I}(CN)_3]_2^{4-}$,[1] and $[Ni^{I}(CN)_3CO]_2^{4-}$.[2] Conclusive evidence for the presence of metal–metal bonds, unsupported by any bridging CO groups, has been given by Dahl, Ishishi, and Rundle[3] for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The strength of such bonds is of interest, especially since it is reported[3] that the Mn–Mn and the Re–Re distance are 2·93

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[1] Griffith and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 295.

[2] Griffith, Cotton, and Wilkinson, *ibid.*, 1959, **10**, 23.

[3] Dahl, Ishishi, and Rundle, *J. Chem. Phys.*, 1957, **26**, 1750.

and 3·02 Å, respectively, compared with distances of ~2·4 and ~2·6 Å expected from sums of estimated covalent radii. Wilson and Shoemaker[4] have concluded that the sole link between the two halves of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ is an Mo–Mo bond with a length of 3·22 Å, which they considered " rather long." In this paper we make an estimate, from thermochemical data, of the energy of the Mn–Mn bond in $Mn_2(CO)_{10}$.

The enthalpy of formation of $Mn_2(CO)_{10}$ has recently been reported[5] as —400·9 kcal./mole. We have measured the enthalpy of sublimation to be 15·0 ± 0·5 kcal./mole. Infrared study[6] has indicated that the molecular structure in the gas phase is the same as that in the crystal. By using the above values of the enthalpy of formation and enthalpy of sublimation of $Mn_2(CO)_{10}$, together with the enthalpy of sublimation of Mn(s)[7] and the enthalpy of formation of CO(g),[7] we calculate the enthalpy of the following process:

$$Mn_2(CO)_{10}(g) = 2Mn(g) + 10CO(g)\colon\ \Delta H^\circ_{298} = 258 \pm 2 \text{ kcal./mole} \quad . \quad . \quad (1)$$

The Mn–Mn bond energy can now be estimated by the following procedure. We first calculate the enthalpies of the following reactions, utilizing the thermochemical data of Cotton, Fischer, and Wilkinson[8,9] and the valency-state promotion energies of Skinner and Sumner.[10] Cr* and Fe* represent the metal atoms in their valency states.[9]

$$1/6\ Cr(CO)_6(g) = 1/6\ Cr^*(g) + CO(g)\colon\ \Delta H = 55{\cdot}3 \text{ kcal./mole}$$
$$1/5\ Fe(CO)_5(g) = 1/5\ Fe^*(g) + CO(g)\colon\ \Delta H = 58{\cdot}3 \text{ kcal./mole}$$

It seems reasonable to expect that the energies of formation of the metal-to-carbon monoxide bonds will change regularly with increasing atomic number of the metal atom provided we consider the metal atom in its promoted state.† Thus we can write, by interpolation of the above:

$$1/5\ Mn(CO)_5(g) = 1/5\ Mn^*(g) + CO(g)\colon\ \Delta H = 56{\cdot}8 \text{ kcal./mole} \quad . \quad . \quad (2)$$

Dr. H. A. Skinner has kindly provided us with an estimate from spectroscopic data of the energy of promotion of the manganese atom to the appropriate valency state, namely, $d^2_{xy}d^2_{xz}d^2_{yz}d_{z^2}$. Using the formula $A(d^7) - 8B + 4C$ (see ref. 10), he calculated:

$$Mn(g) = Mn^*(g)\colon\ \Delta H = 171{\cdot}8 \pm 5{\cdot}8 \text{ kcal./mole} \quad . \quad . \quad . \quad . \quad (3)$$

Subtracting 1/5 of eqn. (3) from eqn. (2), we obtain:

$$1/5\ Mn(CO)_5(g) = 1/5\ Mn(g) + CO\colon\ \Delta H = 22{\cdot}4 \pm 1{\cdot}2 \text{ kcal./mole} \quad . \quad . \quad (4)$$

Then, subtracting ten times eqn. (4) from eqn. (1), we finally obtain:

$$Mn_2(CO)_{10}(g) = 2\ Mn(CO)_5(g)\colon\ \Delta H = 34 \pm 13 \text{ kcal./mole}$$

Most of the uncertainty (±12 kcal./mole) comes, of course, from the uncertainty in the promotion energy of the manganese atom.

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† No particular regularity is to be expected if we consider metal atoms in their ground states. We thank Professor C. D. Coryell for a helpful discussion in which he raised this point. It is also possible that, since the hybridization of the Mn atoms in $Mn_2(CO)_{10}$ is quite similar to that of Cr in $Cr(CO)_6$, it might be better to assume for the enthalpy of equation (2) 55·3 kcal./mole. If this is done, the final Mn–Mn bond energy derived is 49 ± 13 kcal./mole which only adds further weight to the subsequent considerations concerning the Mn–Mn bond length. It should of course be obvious that the enthalpy of equation (2) is at the same time the least certain quantity involved in the calculation and the one to which the final result is most sensitive owing to the fact that it is ultimately multiplied by ten. However, we believe that the answer obtained is of some value since it seems unlikely that the enthalpy of equation (2) should be far from a figure of 55 to 57 kcal./mole.

[4] Wilson and Shoemaker, *J. Chem. Phys.*, 1957, **27**, 809.

[5] Good, Fairbrother, and Waddington, *J. Chem. Phys.*, 1958, **62**, 853.

[6] Cotton, Liehr, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **2**, 141.

[7] Selected Values of Chemical Thermodynamic Properties, U.S. Nat. Bur. Standards, Circular 500. All heats used in this paper are at 25°c.

[8] Cotton, Fischer, and Wilkinson, *J. Amer. Chem. Soc.*, 1956, **78**, 5168.

[9] *Idem, ibid.*, 1959, **81**, 800.

[10] Skinner and Sumner, *J. Inorg. Nuclear Chem.*, 1957, **4**, 245.

Unfortunately, the limits of error are so great that detailed discussion of the significance of this result would be unwarranted. If, however, the true value is 34 kcal./mole or higher, one might question the idea of the Mn–Mn bond being " unusually long." Perhaps the assumed covalent radii are too short, by something approaching 0·25 Å. It seems difficult to believe that a bond between such heavy atoms, which is ~0·5 Å longer than it " ought " to be, could be as strong as 34 kcal./mole. Thus this work might further suggest that the " normal " covalent radii assumed for zerovalent metals of the transition group (such as those used in estimating the multiple bond character in metal-to-CO bonds) may in fact be too small. Wilson and Shoemaker[4] implied that the long Mo–Mo bond in $[(\pi\text{-}C_5H_5Mo(CO)_3]_2$ may be influenced by steric strain, but here also the correctness of the " expected " bond length might be questioned. Further studies of bond energies and bond lengths in metal carbonyls, their derivatives, and related compounds should be worthwhile.

Thermal decomposition of $Mn_2(CO)_{10}$ to Mn and CO made the determination of the vapour pressures somewhat laborious since corrections for the pressure of carbon monoxide were required. However, this decomposition might possibly provide further information about the Mn–Mn bond strength, and a kinetic study is in progress.

The heats of sublimation of $Re_2(CO)_{10}$ and several other carbonyls have been measured and will be reported soon.

EXPERIMENTAL

A sample of $Mn_2(CO)_{10}$ of high purity, originally prepared in the laboratories of the Ethyl Corporation, was used in this study. It was from the same batch as was used in the measurement of the heat of combustion,[5] and we are indebted to Dr. Guy Waddington, formerly of the Bureau of Mines, for supplying this material.

The vapour pressures were measured at various temperatures in the range 102—146° c and it was found that, even at the lower temperature, $Mn_2(CO)_{10}$ slowly decomposes with the formation of carbon monoxide. This was allowed for by quickly cooling the apparatus after measurement of the pressure in the system at an elevated temperature, T_2, and measuring the carbon monoxide pressure at room temperature, T_1, after the apparatus had attained thermal equilibrium. The ideal gas law being assumed valid at such low pressures of carbon monoxide (0·5—12 mm.), the vapour pressure of $Mn_2(CO)_{10}$ was obtained by subtracting the product of the ratio T_2/T_1 and CO pressure at T_1 from the total pressure at T_2.

Pressures were measured with a high-sensitivity double spoon gauge[11] as a null indicator which was connected (see Figure) to a closed-tube (13 mm. int. diam.) mercury manometer mounted against a mirrored scale. Pressure readings obtained from both a cathetometer and the mirrored scale never differed by more than 0·1 mm. Hg.

The sample chamber (SC) was prepared by subliming the carbonyl under a high vacuum into a break-seal tube which was then joined to the gauge at A as shown in the figure. After the gauge had been connected to the pumping system by means of tubing B–C and the gauge to the envelope with break-seal E, the entire apparatus was evacuated to 2×10^{-3} mm. Hg. The sample chamber was then opened magnetically with a glass-enclosed iron plunger, and evacuated for several minutes to insure removal of any carbon monoxide which might have been formed in sealing off the sample chamber. The sample chamber was then cooled to −78°, and the area at B warmed with a stream of hot air in order to remove any carbonyl deposited in the area which would be decomposed on sealing at B.. The tube was then sealed at B and the section of tubing B–C removed. This procedure for mounting of the samples ensured the absence of residual carbon monoxide at the beginning of the measurements.

The gauge was then surrounded by an oil-bath which was provided with heaters, stirrer, thermoregulator, and thermometer. The temperature of the bath was held constant to within 0·5° over the range 100—170°. The gauge was balanced by admitting or removing air to the envelope through stopcock D until the pointer returned to the null position. This was easily accomplished by observing the reference point and pointer through a telescope fitted with a micrometer eyepiece. After complete measurement of a sample, the pressures in the sample

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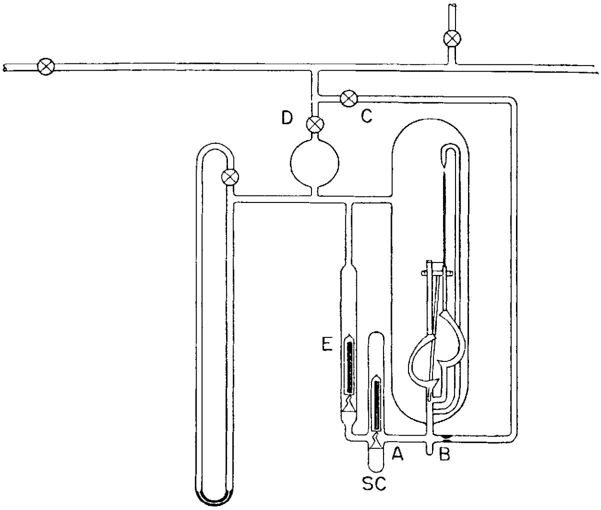
[11] Monchamp, Bannister, and Cotton, *Rev. Sci. Instr.*, 1959, **30**, 945.

chamber and envelope were equalized through break-seal E and the gauge was then detached and cleaned for the next sample.

Diagram showing the attachment of sample chamber and gauge to the vacuum-system.



Three separate samples gave values of 14·9, 15·0, and 15·2 kcal./mole for the heat of sublimation of $Mn_2(CO)_{10}$. The equation for the line best fitting all of the data is: $\log_{10} p$ (mm.) = $9{\cdot}2251 - 3262{\cdot}64/T$.

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