

The Mechanism of Reactions of Manganese Decacarbonyl

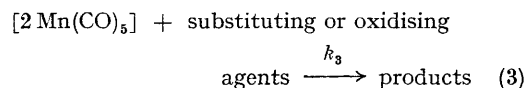
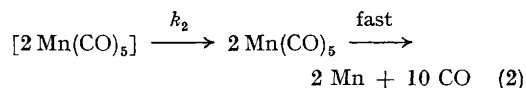
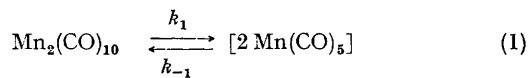
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ON the basis of preparative studies, Wawersik and Basolo recently suggested¹ that substitution reactions of manganese decacarbonyl with phosphines proceed by a mechanism involving dissociation of carbon monoxide as the rate-determining step, and that fission of the Mn-Mn bond does not occur, even at 200°. Subsequent kinetic studies have been interpreted in the same way.² Recent mass-spectroscopic studies³ lead, however, to a value of 19 kcal./mole for the Mn-Mn bond dissociation energy, and this suggests that a reaction mechanism involving Mn-Mn bond fission should be energetically possible.

We have studied the kinetics of reactions of manganese decacarbonyl (in xylene, n-octane, or decalin) with triphenylphosphine and iodine, and also the kinetics of decomposition, both in the presence and absence of oxygen. Ultraviolet and infrared spectrophotometric techniques were used to follow the reactions. The results are all in quantitative agreement with a reaction scheme given in equations (1)–(3), which involves Mn-Mn bond fission as the primary step. $[2 \text{ Mn}(\text{CO})_5]$ represents a pair of manganese pentacarbonyl

radicals, formed by homolytic fission of the Mn-Mn bond, and trapped in a solvent cage.⁴



These radical-pairs can then react in a variety of ways, *viz*: (i) recombination, (ii) diffusion out of the solvent cage followed by rapid decomposition involving complete loss of carbon monoxide, (iii) substitution of carbon monoxide by triphenylphosphine to give a mono- or di-substituted product, depending on whether one or two phosphine molecules react with the radical-pair before recombination, (iv) oxidation by oxygen followed by decomposition with complete loss of carbon

monoxide, (v) oxidation by iodine to form $\text{Mn}(\text{CO})_5\text{I}$ which subsequently decomposes.

This mechanism leads to a rate law given in equation (4)

$$-\frac{d[\text{Mn}_2(\text{CO})_{10}]}{dt} = \frac{k_1\{k_2/k_{-1} + (k_3/k_{-1})[\text{X}]\}[\text{Mn}_2(\text{CO})_{10}]}{1 + k_2/k_{-1} + (k_3/k_{-1})[\text{X}]} \quad (4)$$

where $[\text{X}]$ is the concentration of substituting or oxidising reagent. When $[\text{X}] = 0$, the observed pseudo-first order rate constant for decomposition of $\text{Mn}_2(\text{CO})_{10}$ would be $k_1(k_2/k_{-1})/(1 + k_2/k_{-1})$. As expected from the rate law, the rate of reaction with triphenylphosphine rises from the decomposition rate at very low concentrations of triphenylphosphine to a limiting rate at high concentrations. From the decomposition and substitution studies in decalin we obtain values of $k_1 = 1.7 \times 10^{-4} \text{ sec.}^{-1}$, $k_2/k_{-1} \sim 0.1$, and $k_3/k_{-1} \sim 6 \times 10^3 \text{ l. mole}^{-1}$, at 115° . The variation with temperature of k_1 gives an activation energy for homolytic fission of the Mn-Mn bond of 36.6 kcal./mole .

During the reaction with triphenylphosphine, the growth of infrared absorption bands due to both $\text{Mn}_2(\text{CO})_9\text{PPh}_3^5$ and $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2^6$ were observed. The initial rate of appearance of $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ was too great to be explained by its formation only from $\text{Mn}_2(\text{CO})_9\text{PPh}_3$, formed as an intermediate. The ratio of di- to mono-substituted product, formed in the early part of the reaction, increased with increasing concentration of phosphine, as would be expected if either one or two phosphine molecules could react with the radical-pair before recombination occurs.

From 60° to 95° the rate of decomposition in non-deoxygenated solvents is about the same as

the rate of reaction with phosphine, but, as the temperature increases, the rate of decomposition becomes less than the rate of substitution and this difference increases with temperature. This can be explained by negative temperature coefficients for k_2/k_{-1} and $(k_3/k_{-1})[\text{O}_2]$ such that the recombination reaction becomes progressively more important as the temperature rises, *i.e.*, there is a substantial activation energy for recombination of the radicals within the radical-pair. This is probably associated with stereochemical rearrangement of the manganese pentacarbonyl unit after bond fission. Measurements of the temperature dependence of k_2/k_{-1} are in progress in order to determine the activation energy for recombination of the radicals, that for diffusion out of the cage being assumed to be about 3 kcal./mole .

The difference between our value of 37 kcal./mole for the activation energy for Mn-Mn bond fission, and Bidinosti and McIntyre's value of 19 kcal./mole for the Mn-Mn bond dissociation energy probably arises from the different states of the manganese pentacarbonyl radicals formed from $\text{Mn}_2(\text{CO})_{10}$ by electron bombardment or by thermal dissociation.

The reaction with iodine produces $\text{Mn}(\text{CO})_5\text{I}$, which subsequently decomposes. The observed pseudo-first order rate constant is of the form $k_{\text{obs}} = k_1 + k_2[\text{I}_2]$. The activation energy for the first order constant is about 38 kcal./mole and for the second order constant is 31 kcal./mole .⁷ We assume that the first order term arises from oxidative attack of I_2 on the $[\text{2 Mn}(\text{CO})_5]$ radical pair.

Similar studies on reactions of $\text{Re}_2(\text{CO})_{10}$ and $\text{MnRe}(\text{CO})_{10}$ are in progress.

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¹ H. Wawersik and F. Basolo, *Chem. Comm.*, 1966, 366.

² H. Wawersik and F. Basolo, private communication.

³ D. R. Bidinosti and N. S. McIntyre, *Chem. Comm.*, 1966, 555.

⁴ J. Franck and E. Rabinowich, *Trans. Faraday Soc.*, 1934, **30**, 120; A. M. North, *Quart. Rev.*, 1966, **20**, 421.

⁵ G. Bor, Symposium on the Structure and Properties of Coördination compounds, Bratislava, Czechoslovakia, September, 1964; M. L. Ziegler, H. Haas, and R. K. Sheline, *Chem. Ber.*, 1965, **98**, 2454.

⁶ A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 1964, 634.

⁷ L. I. B. Haines, unpublished work.