Reaction Mechanisms of Metal–Metal-bonded Carbonyls. Part 17.[1] Reactions of Octacarbonylbis(triphenyl phosphite)dimanganese(*Mn–Mn*)

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The kinetics have been studied of the reactions in decalin of the complex $[\{Mn(CO)_4[P(OPh)_3]\}_2]$ with oxygen, carbon monoxide, triphenylphosphine, and triphenyl phosphite. The dependence of the rate of reaction with oxygen on the concentration of complex is characteristic of reversible homolytic fission of the Mn–Mn bond as the major primary reaction step. The half-order nature of the decomposition of the complex in the presence of free $P(OPh)_3$ supports this. A value of 151.0 ± 2.1 kJ mol^{-1} is assigned to the activation enthalpy for homolytic fission, and the effect of the two phosphite substituents on the kinetic strength of the Mn–Mn bond is small in contrast to the effect of two triphenylphosphine substituents.

EVIDENCE has recently been adduced for initial, reversible, homolytic fission of the metal–metal bonds in thermal decompositions and substitutions of some dimetal carbonyls [2,3] and their substituted derivatives.[4,5] In order to establish how widely this mechanism operates, and because kinetic parameters for homolytic fission provide a kinetic measure of the strengths of the

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[2] J. P. Fawcett, A. J. Poë, and K. R. Sharma, *J. Amer. Chem. Soc.*, 1976, **98**, 1401.

[3] J. P. Fawcett and A. J. Poë, *J.C.S. Dalton*, 1976, 2039.

[4] D. G. DeWit, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, 1976, 528.

[5] J. P. Fawcett, R. A. Jackson, and A. J. Poë, *J.C.S. Chem. Comm.*, 1975, 733.

metal–metal bonds, reactions of several substituted dimanganese carbonyl complexes have been studied and we report here results for the axially substituted complex $[\{Mn(CO)_4[P(OPh)_3]\}_2]$.

EXPERIMENTAL AND RESULTS

The complex $[\{Mn(CO)_4[P(OPh)_3]\}_2]$ was prepared from decacarbonyldimanganese (Strem Chemicals) by essentially the method of Wawersik and Basolo.[6] It was purified by repeated recrystallisation from dichloromethane by addition of methanol, and was characterised by its principal i.r. band in the C–O stretching region [6] at 1 983 cm^{-1} (molar absorbance coefficient, ε, 1.6×10^4 dm^3 mol^{-1} cm^{-1}). A band in the near u.v. at 358 nm (ε 2.8×10^4 dm^3 mol^{-1} cm^{-1}) with a shoulder at 408 nm was also shown by solutions of the complex in decalin. Other reagents used, and procedures for the kinetic runs, have been described in preceding papers in this series. The extent of reaction was usually determined by measuring the intensity of the band at 1 983 cm^{-1} in cells of suitable path length. It decreased to zero in most reactions. The decreasing absorbance in the near u.v. (340—370 nm) was occasionally followed.

Reaction of $[\{Mn(CO)_4[P(OPh)_3]\}_2]$ *with Oxygen.*—Reaction under an atmosphere * of pure oxygen proceeded cleanly with complete disappearance of all C–O stretching bands when the concentration of the complex was $\lesssim 5 \times 10^{-4}$ mol dm^{-3}. First-order rate plots were linear up to 80—90% completion of reaction. With higher concentrations ($>10^{-3}$ mol dm^{-3}), however, i.r. bands at 2 025 and 2 001 cm^{-1} grew in intensity throughout the reaction. These bands can be ascribed to the complex $[Mn_2(CO)_9\{P(OPh)_3\}]$,[6] the yield of which was never more than *ca.* 10%. Reaction in the presence of added triphenyl phosphite occurred without formation of this product but the rates were unaffected. As the initial concentration of complex, c_0, increased the first-order rate plots became more curved, gradients increasing with time. Corresponding half-order rate plots were also curved, the gradients decreasing with time. The apparent first-order rate constants, k_0, obtained from the initial gradients of the first-order rate plots, decreased steadily with increasing values of c_0 (Table 1). The data were therefore also expressed as initial rates $R_0 = k_0 c_0$. Activation parameters (Table 1) were calculated by a least-squares analysis of the dependence of $\log(k_0/T)$ on $1/T$ for all values of k_0 found when $c_0 = ca.\ 4 \times 10^{-4}$ mol dm^{-3}

Reactions under atmospheres of 5% oxygen (in O_2–N_2 mixtures) were more complicated, more interference from formation of $[Mn_2(CO)_9\{P(OPh)_3\}]$ occurring. This was not prevented by addition of free $P(OPh)_3$. Reliable values of absorbance at the end of the reaction could not be obtained because the monophosphite product itself underwent slow decomposition, and the rate data were much less reproducible and precise. However, the values of k_0 decreased with increasing c_0 and were all substantially lower than those for corresponding reactions under pure oxygen.

Reaction in the Presence of Triphenyl Phosphite.—Heating the complex in decalin under atmospheres of argon or nitrogen and in the presence of added $P(OPh)_3$ led to complete disappearance of the band at 1 983 cm^{-1} without the growth of any other bands in the C–O stretching region: At higher concentrations of complex visible amounts of a brown precipitate were formed and had to be filtered off before the spectra of the reaction mixtures were measured.

TABLE 1

Kinetic data for decomposition of $[\{Mn(CO)_4[P(OPh)_3]\}_2]$ in decalin under oxygen [a]

θ_c / °C	$10^5 c_0$ / mol dm^{-3}	$10^4 k_0$ / s^{-1}	$10^8 R_0$ / mol dm^{-3} s^{-1}	$10^8 R_0$ (calc.) / mol dm^{-3} s^{-1}	Δ [b]
127.0	330 [c]	15.1	498	490	−1.6
	295	15.2	448	456	1.8
	161	18.2	293	301	2.7
	90.5	23.0	196	197	0.5
	42.4	27.6	117	108	−8.3
	42.0 [c]	26.0	109	107	−1.9
	39.0 [d]	26.3	103	100	−3.0
	14.6	29.6	42.4	42.2	−0.5
	6.00	29.8	17.9	18.3	2.2
	5.37	31.2	16.8	16.4	2.4
	4.36	30.1	13.1	13.8	5.0
122.0	43.1	17.8			
	34.4	17.8			
120.0	40.0	13.8			
117.0	33.8	9.23			
	33.6	9.63			
115.0	40.0	7.41			
107.0	40.0	2.43			
102.0	33.6	1.43			
	30.8	1.38			
95.0	40.0	5.25			
92.0	44.9	3.30			
	44.8	3.30			

$\Delta H^\ddagger = 151.0 \pm 2.1$ kJ mol^{-1}; [e] $\Delta S^\ddagger = 81.4 \pm 5.4$ J K^{-1} mol^{-1}; [e] $\sigma(k_0) = \pm 8.6\%$ [f]

[a] $[P(OPh)_3] = 0$, except where indicated. [b] $100[R_0(calc.) - R_0]/R_0(calc.)$. [c] $[P(OPh)_3] = 0.6$ mol dm^{-3}. [d] $[P(OPh)_3] = 0.2$ mol dm^{-3}. [e] From least-squares analysis of values of k_0 with $10^5 c_0 = 30$—45 mol dm^{-3}. Uncertainties are standard deviations corrected for the number of degrees of freedom. [f] $\sigma(k_0)$ = Standard deviation of an individual measurement.

TABLE 2

Half-order rate constants for decomposition of $[\{Mn(CO)_4[P(OPh)_3]\}_2]$ in decalin under argon at 117.0 °C

$10^5 c_0$ / mol dm^{-3}	$10^2[P(OPh)_3]$ / mol dm^{-3}	$10^6 k_{obs.}$ / $mol^{\frac{1}{2}}$ $dm^{-\frac{3}{2}}$ s^{-1}
250	10.0	1.50
105	4.4	1.44
84.1	4.1	1.46
56.1	10.0	1.46
46.6	19.8	1.67
45.4	9.6	1.35
43.8	2.4	1.32
43.3	4.5	1.69
43.2	10.0	1.56
29.3	3.9	1.59
16.6	4.4	1.51
12.7	10.0	1.47
8.25	10.0	1.55
8.14	4.1	1.48
6.47	4.1	1.25
2.92	4.4	1.21

$10^8 k_{av.} = 147 \pm 4$ $mol^{\frac{1}{2}}$ $dm^{-\frac{3}{2}}$ s^{-1}; $\sigma(k_{obs.}) = \pm 9.2\%$.

First-order rate plots were all badly curved, but half-order ones were linear for up to *ca.* 80% completion of reaction. The half-order rate constants (Table 2) are independent of c_0 and $[P(OPh)_3]$.

Reaction with Carbon Monoxide.—Reaction under atmospheres of pure CO, or of CO–N_2 mixtures, was accompanied

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* Throughout this paper: 1 atm = 76 cmHg; 1 mmHg ≈ 13.6 × 9.8 Pa.

[6] H. Wawersik and F. Basolo, *Inorg. Chim. Acta*, 1969, **3**, 113.

by the growth of i.r. bands at 2 025s, 2 001vs, and 1 975(sh) cm^{-1}, characteristic of [$Mn_2(CO)_9\{P(OPh)_3\}$].[6] The intensity of these bands remained constant, after completion of the reaction, for a sufficient time to show that the product was quite stable towards replacement of the remaining $P(OPh)_3$ ligand. The kinetics were followed by measuring the *decreasing* absorbance at 1 983 cm^{-1}, a wavenumber on the side of a product band where precise measurement of A_∞ was difficult. The changing absorbance during the reaction was therefore plotted according to Swinbourne's method,[7] the gradients of plots of A_t against $A_{t+\Delta t}$ providing approximate values of first order rate constants, and the absorbance when $A_t = A_{t+\Delta t}$ being A_∞. When these values of A_∞ were used, conventional first-order plots were linear for *ca.* 90% reaction. The rate constants (Table 3) were independent of c_0, of the partial pressure, p_{CO}, of CO in the CO–N_2 mixtures, of the presence of very small amounts of added $P(OPh)_3$, and of the presence of oxygen.

TABLE 3

Kinetic data for reaction of [$\{Mn(CO)_4[P(OPh)_3]\}_2$] with carbon monoxide in decalin

$\frac{\theta_c}{°C}$	$\frac{10^5 c_0}{mol\ dm^{-3}}$	$y(CO)$ [a]	$\frac{10^4 k_{obs}}{s^{-1}}$
127.0	865	1.0	21.8
	48.2	1.0	23.1
	46.4	1.0	21.3
	41.5	1.0	21.2
	41.5	1.0	21.9
	24.4	1.0	22.3
	42.1	0.50	23.1
	42.1	0.25	21.3
	41.5	0.15	22.0
	41.5	0.15	21.8
	40.0	0.15	22.2
	99.0	0.05	19.4
	75.0	0.05	21.9
	43.0	0.05	22.0
	40.0	0.05	21.0
	40.0	0.05	20.4
	40.0	0.05	21.3 [b]
	40.0	0.05	21.6 [c]
	36.8	0.05	20.6
	23.8	0.05	19.0
	22.6	0.05	21.6
122.0	41.8	1.0	15.4
	40.6	1.0	13.2
	44.2	0.50 [d]	14.2
120.0	40.0	1.0	11.0
117.0	43.3	1.0	8.25
	43.2	1.0	8.25
	41.1	1.0	8.55
110.0	40.0	1.0	3.31
102.0	44.1	1.0	1.11
	43.4	1.0	1.10
100.0	40.0	1.0	0.79
92.0	47.1	1.0	0.299
	43.4	1.0	0.313
90.0	40.0	1.0	0.230

$\Delta H^\ddagger = 149.3 \pm 2.5$ kJ mol^{-1}; [e] $\Delta S^\ddagger = 75.5 \pm 6.5$ J K^{-1} mol^{-1}; $\sigma(k_{obs.}) = \pm 9.5\%$

[a] Mol fraction of CO in CO–N_2 mixture. [b] [$P(OPh)_3$] = 6.4×10^{-4} mol dm^{-3}. [c] [$P(OPh)_3$] = 3.2×10^{-4} mol dm^{-3}. [d] Mol fraction of CO in CO–O_2 mixture. [e] Calculated by including the average of $k_{obs.}$ for reaction with PPh_3 at 127 °C (Table 4) and using average value of $k_{obs.}$ for reaction with CO at 127 °C.

Activation parameters were calculated by least-squares analysis. The average value of $k_{obs.}$ for reaction with PPh_3 at 127 °C (see below) was included in these calculations. Only the average value [$(21.3 \pm 0.3) \times 10^{-4}$ s^{-1}] of the rate constant at 127 °C was used so as to prevent undue weighting of the data at 127 °C due to their much greater number compared with those at other temperatures.

Reaction with Triphenylphosphine.—Reaction in decalin with 0.2 mol dm^{-3} PPh_3 led to the growth of a strong i.r. band at 1 963 cm^{-1} that is characteristic of the complex [$\{Mn(CO)_4(PPh_3)\}_2$], the band at 1 983 cm^{-1} disappearing and no intermediate species being detected. Excellent first-order rate plots were obtained. As [PPh_3] was decreased the product spectrum became more complex, a strong band at 1 975 cm^{-1} with a shoulder at 1 988 cm^{-1} becoming increasingly prominent and being assigned to the bis(axial) mixed-ligand complex [$Mn_2(CO)_8\{P(OPh)_3\}(PPh_3)$]. The growth of the band at 1 975 cm^{-1} and its shoulder at 1 988 cm^{-1} made the Swinbourne method necessary for the estimation of A_∞ at 1 983 cm^{-1}, but good first-order rate plots were then obtained. Rate constants (Table 4) are independent of [PPh_3] down to $<10^{-2}$ mol dm^{-3}. The average value of the rate constant at 127 °C [$(22.2 \pm 0.3) \times 10^{-4}$ s^{-1}] is indistinguishable from that for reaction with CO.

TABLE 4

First-order rate constants for reaction of [$\{Mn(CO)_4[P(OPh)_3]\}_2$] with PPh_3 in decalin at [complex] = 4.0×10^{-4} mol dm^{-3} and 127.0 °C

$10^2[PPh_3]$/mol dm^{-3}	20.0	20.0	19.0	10.0	6.3
$10^4 k_{obs.}$/s^{-1}	22.2	22.0	22.0	22.5	22.1
$10^2[PPh_3]$/mol dm^{-3}	4.5	2.0	1.0	1.0	0.20
$10^4 k_{obs.}$/s^{-1}	22.0	22.7	22.0	22.3	20.4

DISCUSSION

Decomposition Reactions.—The increase with c_0 of the curvature of the first-order rate plots for decomposition under oxygen, and the concomitant decrease in the apparent first-order rate constants, are qualitatively characteristic of initial reversible fragmentation of the complex, recombination of the fragments competing more successfully with their reaction with oxygen the higher the concentration of complex. By analogy with the corresponding reaction [2] of [$Mn_2(CO)_{10}$], we propose the mechanism shown in equations (1)—(3) for which rate equation (4) applies.[2] R_1 is the limiting rate, $k_1 c_0$, and $c = k_2/k_{-1}^{\frac{1}{2}} + (k_3/k_{-1}^{\frac{1}{2}})[O_2]$. Equation (4) can be rearranged to (5). A plot of k_0 against $k_0^2 c_0$ is shown in the Figure, and leads to $k_1 = 31.7 \times 10^{-4}$ s^{-1} and c = 4.2×10^{-3} mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$ s$^{-\frac{1}{2}}$ at 127 °C. These values were

$$[\{Mn(CO)_4[P(OPh)_3]\}_2] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2[Mn(CO)_4\{P(OPh)_3\}] \quad (1)$$

$$[Mn(CO)_4\{P(OPh)_3\}] \xrightarrow{k_2} \text{decomposition} \quad (2)$$

$$[Mn(CO)_4\{P(OPh)_3\}] + O_2 \xrightarrow{k_3} \text{decomposition} \quad (3)$$

$$2R_0/(R_1 - R_0)^{\frac{1}{2}} = c \quad (4)$$

$$k_0 = k_1 - 4(k_0/c)^2 c_0 \quad (5)$$

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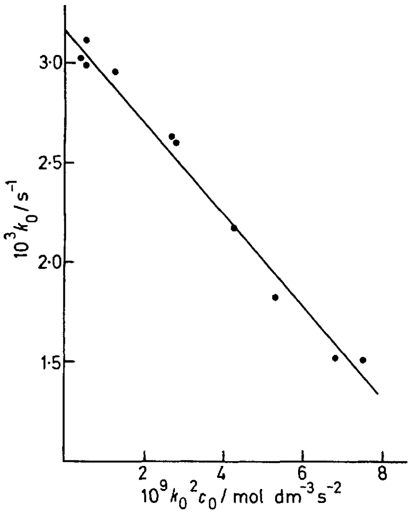
[7] E. S. Swinbourne, 'Analysis of Kinetic Data,' Nelson, London, 1971, p. 81.

used to calculate values of R_0 (Table 1) for each value of c_0 used. The values of $100|[R_0(\text{calc.}) - R_0]|/R_0(\text{calc.})$ have a mean of 2.7% which shows that the data are in excellent quantitative agreement with the proposed mechanism. The fact that even large amounts of added $P(OPh)_3$ do not retard the reaction shows that dissociation of $P(OPh)_3$ at any stage does not play a kinetically important role in the reaction, just as dissociation of CO is not important in the decomposition of $[Mn_2(CO)_{10}]$, at least at lower temperatures.[2]

The apparent first-order rate constants for $c_0 = ca.$ 4×10^{-4} mol dm^{-3} at 127 °C are very close to the limiting value, so the activation parameters in Table 1 will correspond very closely to those for homolytic fission.



Dependence of apparent first-order rate constant (k_0) for decomposition in decalin under oxygen on initial concentration of complex, c_0, at 127 °C

The excellent constancy of the half-order rate constants for decomposition [under an inert atmosphere and in the presence of free $P(OPh)_3$] over almost a 100-fold range of c_0 and a 10-fold range of $[P(OPh)_3]$, and the absence of any carbonyl-containing products, suggests that the reaction can be described very satisfactorily by equations (1) and (2). Reaction (2) cannot be $P(OPh)_3$-dissociative or -associative and probably occurs by initial CO dissociation. The observed half-order rate constants will be given by $0.5k_1^{\frac{1}{2}}(k_2/k_{-1}^{\frac{1}{2}})$.[2] Since $k_1 =$ *ca.* 1×10^{-3} s^{-1} at 117 °C (Table 1), $k_2/k_{-1}^{\frac{1}{2}} =$ *ca.* 10^{-4} mol$^{\frac{1}{2}}$ dm$^{-\frac{3}{2}}$ s$^{-\frac{1}{2}}$. This value is unlikely to be greatly changed by a 10 °C increase in temperature and the value of c found at 127 °C must, therefore, correspond to $(k_3/k_{-1}^{\frac{1}{2}})[O_2]$ so that $k_3/k_{-1}^{\frac{1}{2}} = 0.7$ dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$ $\{[O_2] =$ *ca.* 6×10^{-3} mol dm^{-3} at 127 °C (ref. 2)$\}$. This is quite close to the corresponding values for the complexes $[M_2(CO)_{10}]$ ($M_2 = Mn_2$, MnRe, or Tc_2) at similar temperatures, as is the value $k_3/k_2 =$ *ca.* 10^4 dm^3 mol^{-1}.[3]

Substitution Reactions.—The rates of substitution of $P(OPh)_3$ by PPh_3 and CO are essentially identical at 127 °C and we conclude that both reactions go by the same mechanism. The rates of substitution by CO are slightly less than those for reaction with O_2 over the whole temperature range used. This does not appear to be because the substitution is occurring at less than its limiting rate, since the rate constants are independent of [CO], $[PPh_3]$, and c_0. Small amounts of added $P(OPh)_3$ have no effect on the rates so retardation by trace amounts of $P(OPh)_3$ present in the sample of complex, or released during reaction, cannot be the cause. Reaction with a mixture of CO and O_2 does not proceed at a rate equal to the sum of the rates with CO and O_2 so the two reactions are not going by two completely independent paths but must have a major path in common. Moreover, the activation parameters for substitution and decomposition are essentially identical and we conclude that homolytic fission is probably a major initial step in the substitutions as well as in the decomposition. This has also been concluded for the reaction of $[\{Mn(CO)_4(PPh_3)\}_2]$ with $P(OPh)_3$ which leads to $[Mn_2(CO)_8\{P(OPh)_3\}(PPh_3)]$ at all concentrations of $P(OPh)_3$.[5] In contrast, reaction of $[\{Mn(CO)_4[P(OPh)_3]\}_2]$ with PPh_3 leads directly to $[\{Mn(CO)_4(PPh_3)\}_2]$ at higher values of $[PPh_3]$ and this must be due to a combination of differences in the steady-state concentrations of $[Mn(CO)_4(PPh_3)]$ and $[Mn(CO)_4\{P(OPh)_3\}]$, caused by the different conditions for the two reactions, as well as to the relative rate constants for combinations of two like or unlike five-co-ordinate radicals.

Effect of Substituents on the Energetics of Homolytic Fission.—It has been shown[8] that substitution of two PPh_3 ligands into $[Mn_2(CO)_{10}]$ appreciably weakens the kinetic strength of the Mn–Mn bond, the activation enthalpy for homolytic fission being lowered by 30 kJ mol^{-1}. This effect has been ascribed[8] mainly to the large size[9] of the phosphine which is such that ligand–ligand repulsion is substantially reduced as the Mn–Mn bond is stretched. The presence of the two $P(OPh)_3$ ligands has almost no effect on the value of $\Delta H^\ddagger$ for homolytic fission, the values for $[Mn_2(CO)_{10}]$ and $[\{Mn(CO)_4[P(OPh)_3]\}_2]$ being 153.8 ± 1.6 * and 151.0 ± 2.1 kJ mol^{-1}, respectively. This is quite consistent with the much smaller cone angle of $P(OPh)_3$.[9]

We thank Erindale College and the National Research Council of Canada for support.

[7/438 *Received, 14th March,* 1977]

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* Recalculated from data in L. I. B. Haines, Ph.D. Thesis, London University, 1968.

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