Reaction Mechanisms of Metal–Metal Bonded Carbonyls. Part 12.[1] Reactions of Decacarbonylmanganeserhenium, Decacarbonylditechnetium, and their Bis(triphenylphosphine) Derivatives

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The kinetics of the following reactions in decalin have been studied: the complexes $[MnRe(CO)_{10}]$ and $[Tc_2(CO)_{10}]$ with triphenylphosphine, $[MnRe(CO)_8(PPh_3)_2]$ and $[Tc_2(CO)_8(PPh_3)_2]$ with carbon monoxide, and decomposition of $[Tc_2(CO)_{10}]$ under oxygen. The results are consistent with initial reversible homolytic fission of the metal–metal bonds so that the activation enthalpies for the rate-limiting steps can be taken as a kinetic measure of the strengths of the metal–metal bonds. Attention is drawn to correlations between the activation enthalpies for the decacarbonyls and spectroscopic parameters related to the bond strengths.

DETAILED studies of reactions of decacarbonyldimanganese[2] and its bis(triphenylphosphine)[3] derivative have provided good kinetic evidence for reversible homolytic fission of the manganese–manganese bond as the initial rate-limiting step. Reaction of decacarbonylmanganeserhenium with oxygen is also consistent with

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[1] Part 11, D. G. DeWit, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, 1976, 528.

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

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

this mechanism.[2] Activation parameters for the homolytic fission process are valuable in providing a kinetic measure of the strength of the metal–metal bonds in such complexes.[4] We report here some studies of other reactions of the complex [$MnRe(CO)_{10}$], of reactions of its bis(triphenylphosphine) derivative, and of reactions of [$Tc_2(CO)_{10}$] and [$Tc_2(CO)_8(PPh_3)_2$] that are all consistent with this mechanism.

EXPERIMENTAL

Preparation of the samples of the complexes [$MnRe(CO)_{10}$] and [$MnRe(CO)_8(PPh_3)_2$] has been described.[5] Decacarbonylditechnetium was prepared from technetium metal (53 mg) according to the published method [6] by conversion into a mixture of oxides, and subsequent carbonylation under pressure (300 atm, 150 °C, 20 h) * in an autoclave in the presence of copper powder. The decacarbonyl was separated from the product mixture by dissolving in diethyl ether followed by evaporation (yield 55 mg, 45%). Identical i.r. spectra and kinetic behaviour were observed for this complex to those of a sample obtained from Pressure Chemical Co. Rubber gloves were worn and other suitable care taken when handling solid samples of this complex, although, because of the low specific activity of the samples and the low energy of the radiation emitted by the ^{99}Tc nuclide, negligible danger was involved apart from that resulting from ingestion.

Other chemicals used, and the procedures for the kinetic runs, have all been described in preceding papers in this series.

RESULTS

Reaction of [$MnRe(CO)_{10}$] *with Triphenylphosphine*.—This reaction occurs at convenient rates in decalin from 110 to 155 °C. At low concentrations of PPh_3, under argon, i.r. bands grew at 2 095w, 2 030m, 1 990s, 1 971m, and 1 949w cm^{-1}. These have been assigned to the complex [$(OC)_5MnRe(CO)_4(PPh_3)$].[5] At higher phosphine concentrations a band at 1 965 cm^{-1} due to the bis-axial complex [5] [$(Ph_3P)(OC)_4MnRe(CO)_4(PPh_3)$] also grew even in the initial stages of the reaction, the relative initial yield of bis : mono complex increasing with increasing phosphine concentration. The kinetics of the reaction were followed by monitoring the decreasing intensity of the band at 2 054 cm^{-1} (ε 6 700 $dm^3\ mol^{-1}\ cm^{-1}$) due to the decacarbonyl. Good first-order rate plots, generally linear for *ca.* 3 half-lives, were obtained and the results are reported in Table 1.

Reactions under carbon monoxide were also studied and the only product found was the monophosphine complex except at the highest phosphine concentration used (0.16 mol dm^{-3}) when some disubstituted product was detected. At phosphine concentrations below *ca.* 0.01 mol dm^{-3} an equilibrium mixture of deca- and nona-carbonyl was obtained, and the three runs at 5.00×10^{-3}, 3.33×10^{-3}, and 2.50×10^{-3} mol dm^{-3} PPh_3 had more than 45% decacarbonyl left at equilibrium. A value of the equilibrium constant $K = [MnRe(CO)_9(PPh_3)][CO]/[MnRe(CO)_{10}][PPh_3] = 0.80$, with a maximum spread of ±0.12, was estimated from the intensities of the i.r. bands and the value [CO] = 4.9×10^{-3} mol dm^{-3} at 140 °C.[7]

One reaction at 155 °C with [PPh_3] = 0.09 mol dm^{-3} was followed under an atmosphere of oxygen. A good first-order rate plot was obtained with $k_{obs.} = 1.21 \times 10^{-3}\ s^{-1}$. This is slightly slower than the corresponding reaction under argon. I.r. bands due to the nonacarbonyl were observed to grow until *ca.* 60% of the decacarbonyl had reacted, after which they decayed. Extensive precipitation of a white solid occurred towards the end of the reaction, and its i.r. spectrum in chloroform was identical with an authentic sample of triphenylphosphine oxide.

TABLE 1

Kinetic data for reaction of [$MnRe(CO)_{10}$] with triphenylphosphine in decalin

θ_c/°C	$10^3[PPh_3]$/mol dm^{-3}	$10^5k_{obs.}/s^{-1}$
155	0.545	41.0 [a]
	1.38	67.6
	10.7	125
	105	136
	139	138
	168	144
	178	133
141.5	117	28.7
140	2.47	23.0
	10.0	23.6
	72.0	24.0
	100	22.8
	125	24.3
	191	24.6
	2.50 [b]	5.51 [c]
	3.33 [b]	9.60 [c]
	5.00 [b]	11.0 [c]
	10.0 [b]	15.2 [c]
	40.0 [b]	19.7
	100 [b]	22.5
	160 [b]	23.9
126.5	91.2	4.81
	146	4.87
125	102	4.03
	147	3.96
110	48.7	0.578
	73.8	0.568
	111	0.553
	149	0.548
	193	0.565

$\Delta H^\ddagger = 162.8 \pm 0.8$ kJ mol^{-1};[d] $\Delta S^\ddagger = 77.4 \pm 2.1$ J K^{-1} mol^{-1};[d] $\sigma(k_{obs.}) = \pm 4.2\%$.[d]

[a] Curved rate plot, initial gradient taken. [b] Under carbon monoxide. [c] From initial gradient of rate plots calculated assuming the reaction went to completion. [d] From least-squares analysis of the limiting values of the rate constants. Uncertainties are standard deviations corrected for the number of degrees of freedom; $\sigma(k_{obs.})$ = standard deviation of an individual measurement.

Reaction of [$MnRe(CO)_8(PPh_3)_2$] *with Carbon Monoxide*.—In decalin at 90—120 °C, under an atmosphere of carbon monoxide, this reaction has been shown to form [$(OC)_5MnRe(CO)_4(PPh_3)$] and [$(Ph_3P)(OC)_4MnRe(CO)_5$] in the ratio *ca.* 3 : 1.[5] No appreciable amount of [$MnRe(CO)_{10}$] is formed. In the presence of added PPh_3 the yield of the Mn–PPh_3 isomer decreased so that at 0.14 mol dm^{-3} PPh_3 it was barely detectable. Under these conditions the reaction approaches an equilibrium mixture for which $K = [(OC)_5MnRe(CO)_4(PPh_3)][PPh_3]/[MnRe(CO)_8(PPh_3)_2][CO] = 1.0 \times 10^2$ at 120.2 °C. At higher partial pressures of carbon monoxide, in the absence of added PPh_3, the

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* 1 atm = 101 325 Pa.

[4] (*a*) J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1973, 267; (*b*) R. A. Jackson and A. J. Poë, *Proc. 16th Internat. Conf. Co-ordination Chem.*, Dublin, 1974, paper 3.20.

[5] J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J. Organometallic Chem.*, 1973, **61**, 315.

[6] J. C. Hileman in 'Preparative Inorganic Reactions,' vol. 1, ed. W. J. Jolly, Interscience, New York, 1964, p. 102.

[7] M. Basato, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, **1974**, 1350.

reaction proceeded at a limiting rate but the rate constants decreased slightly as $p(CO)$ was reduced below *ca.* 0.3. However, in the absence of PPh_3 and CO reaction occurred to form $[(OC)_5MnRe(CO)_4(PPh_3)]$ in about the same yield (70%) as under an atmosphere of carbon monoxide, but the yield of the Mn–PPh_3 isomer was considerably reduced and a new i.r. band at 1 941 cm^{-1} was observed. Moreover, the rate was approximately equal to the limiting rate although the rate plot was linear only for *ca.* 1 half-life after which the gradient decreased markedly. Under these conditions the reaction is evidently complicated by decomposition products. In the absence of such complications good first-order rate plots, linear for *ca.* 3 half-lives, were obtained and the data are reported in Table 2.

TABLE 2

Kinetic data for reaction of $[MnRe(CO)_8(PPh_3)_2]$ with carbon monoxide in decalin.

$[complex] = 3.5 \times 10^{-4}$ mol dm^{-3}

θ_c/°C	$p(CO)$ [a]	$10^3[PPh_3]$/ mol dm^{-3}	$10^5k_{obs.}/s^{-1}$
120.2	1.0	0	177
	1.0	0	165
	0.66	0	168
	0.27	0	170
	0.13	0	155
	0.051	0	119
	0.021	0	145
	0	0	156
	1.0	9.83	89.5
	1.0	48.8	31.7 [b]
	1.0	140	17.4 [b]
110.2	1.0	0	46.4
100.4	1.0	0	12.9
90.1	1.0	0	3.02
	1.0	0	3.14

$\Delta H^{\ddagger} = 155.2 \pm 1.3$ kJ mol^{-1}; $\Delta S^{\ddagger} = 94.6 \pm 3.8$ J K^{-1} mol^{-1}; $\sigma(k_{obs.}) = \pm 3.0\%$.

[a] Mole fraction of carbon monoxide in the CO–N_2 mixture above the solution. [b] For approach to equilibrium mixture.

Reaction of $[Tc_2(CO)_{10}]$ *with Triphenylphosphine.*—Reactions in decalin at 100—150 °C proceeded smoothly. The i.r. band at 2 058 cm^{-1} (ε 6×10^3 dm^3 mol^{-1} cm^{-1}) due to the decacarbonyl steadily decreased in intensity while bands at 2 098 (2×10^3), 2 028 (3×10^3), 1 999 (22×10^3), 1 979 (3×10^3), and 1 946 (5×10^3 dm^3 mol^{-1} cm^{-1}) cm^{-1} grew and then decayed during the reaction. The numbers in parentheses are approximate absorption coefficients estimated from equilibrium studies (see below) and these bands can be assigned to the complex $[Tc_2(CO)_9(PPh_3)]$. Another band at 1 964 cm^{-1} (ε 18×10^3 dm^3 mol^{-1} cm^{-1}) also grew and remained with constant intensity at the end of the reaction, the quoted absorption coefficient being based on the assumption that no decomposition has occurred. This band can be assigned to the complex $[\{Tc(CO)_4(PPh_3)\}_2]$. At low phosphine concentrations ($<10^{-3}$ mol dm^{-3}) and under argon the nonacarbonyl was present in 50% yield by the time the decacarbonyl had completely reacted, but at higher phosphine concentrations ($>10^{-2}$ mol dm^{-3}) less nonacarbonyl was formed and the bisphosphine complex was the only final product. Under an atmosphere of carbon monoxide and at 140 °C, the monophosphine complex is stabilised relative to the disubstituted product and an equilibrium mixture of the two was found. When $[PPh_3] = 5.76 \times 10^{-3}$ and 32.6×10^{-3} mol dm^{-3} the equilibrium constant $K = [Tc_2(CO)_8(PPh_3)_2][CO]/[Tc_2(CO)_9(PPh_3)][PPh_3] =$ *ca.* 0.2 at 140 °C.

Good first-order rate plots, linear for *ca.* 3 half-lives, were obtained by monitoring the decreasing intensity of the band at 2 058 cm^{-1} and the kinetic data are shown in Table 3.

TABLE 3

Kinetic data for reactions of $[Tc_2(CO)_{10}]$ in decalin.
$[complex] = 3.2 \times 10^{-4}$ mol dm^{-3}

θ_c/°C	10^3[PPh] [a]/ mol dm^{-3}	$10^5k_{obs.}$ [b]$/s^{-1}$	$p(O_2)$ [c]	$10^5k_{obs.}$ [d]$/s^{-1}$
170			0	7.26
			0	0.72 [e]
155			0	5.08
150	110	310		
	123	314		
140	0.687	72.0	0	2.5
	3.12	93.1	0.21	25.8
	9.06	102	0.56	45.0
	68.3	106	1.00	72.2
	182	107		
	5.76	61.3 [e]		
	32.6	89.3 [e]		
	107	91.4		
	179	97.0		
130	184	31.4	1.00	26.6
119.8	175	9.06	0.21	7.25
	186	9.14	1.00	8.55
109.9	194	2.57	1.00	2.63
100.1	189	0.627	0.21	0.630
			1.00	0.613

$\Delta H^{\ddagger} = 160.1 \pm 0.8$ kJ mol^{-1};[f] $\Delta S^{\ddagger} = 82.6 \pm 2.1$ J K^{-1} mol^{-1};[f] $\sigma(k_{obs.}) = \pm 4.0\%$.[f]

[a] Not applicable to decomposition reactions for which $[PPh_3] = 0$. [b] For substitution. [c] Mole fraction of oxygen in O_2–N_2 mixtures above the reaction solution. [d] Apparent first-order rate constants for decomposition. [e] Under an atmosphere of carbon monoxide. [f] From substitution data.

Decomposition of $[Tc_2(CO)_{10}]$ *under Oxygen or Argon.*—Reaction under an atmosphere of oxygen proceeded smoothly in decalin between 100 and 150 °C. No bands attributable to metal carbonyl products were observed to grow but a broad peak at *ca.* 1 720 cm^{-1} was seen at the end of the reaction and can probably be assigned to products of oxidation of the solvent.[2] Below 120 °C the apparent pseudo-first-order rate constants, obtained by monitoring the decreasing intensity of the band at 2 058 cm^{-1}, are identical with those for the corresponding substitution reaction, but as the temperature increased the rate constants for reaction with oxygen became relatively lower. At 140 °C the reaction under air was much slower than that under oxygen and the first-order rate plots were curved, the gradient increasing substantially after *ca.* 1 half-life.

Decomposition under argon between 140 and 170 °C was also followed, and a product was found to grow as shown by the appearance of bands at 2 035m, 1 936s, and 1 724w cm^{-1}. (These bands are almost identical with those observed to grow during the corresponding reaction of decacarbonyldirhenium.[8]) First-order rate plots were obtained by monitoring loss of $[Tc_2(CO)_{10}]$ and showed pronounced curvature, the gradients increasing with time. The values of the apparent first-order rate constants obtained from the initial gradients are given in Table 3 (together with the data for decomposition under oxygen). Corresponding values obtained by monitoring the growth of product bands were essentially identical. Decomposition was also observed at 170 °C under carbon monoxide when no carbonyl bands were seen to grow.

Reactions of $[\{Tc(CO)_4(PPh_3)\}_2]$ *in Decalin.*—Owing to the

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[8] J. P. Fawcett, Ph.D. Thesis, London University, 1973.

small amount of $[Tc_2(CO)_{10}]$ available it was not possible to isolate the bisphosphine complex but some kinetic studies were made by using samples prepared *in situ*. Reaction of the decacarbonyl (2.5×10^{-5} mol dm^{-3}) with a five-fold excess of phosphine under argon (140 °C, 3 h) produced a 3 : 1 mixture of the bis- and mono-substituted complexes. After cooling and replacing the argon atmosphere with one of carbon monoxide the temperature was raised and the disappearance of the bis complex was monitored by following the decreasing intensity of the band at 1 964 cm^{-1}. Good linear first-order rate plots were obtained and the bands due to the complex $[Tc_2(CO)_9(PPh_3)]$ increased in intensity. At higher temperatures, bands due to the decacarbonyl were also observed to grow. One reaction was followed at 130 °C after addition of just enough iodine at room temperature to precipitate the free phosphine present as the iodotriphenylphosphonium iodide salt. No reaction of the iodine with the technetium complexes was observed. The rate data are shown in Table 4.

TABLE 4

Kinetic data for reaction of $[\{Tc(CO)_4(PPh_3)\}_2]$ with carbon monoxide in decalin

$[Tc_2(CO)_8(PPh_3)_2] = 2.5 \times 10^{-4}$ mol dm^{-3}, $[PPh_3] = 9.7 \times 10^{-4}$ mol dm^{-3}, $p(CO) = 1.00$ [a]

θ_c/°C	140	130 [b]	130	119.6	110.8
$10^4 k_{obs.}$/s^{-1}	46.6	17.6	19.0	5.51	2.08

$\Delta H^{\ddagger} = 138.0 \pm 2.2$ kJ mol^{-1}; [c] $\Delta S^{\ddagger} = 42.3 \pm 5.4$ J K^{-1} mol^{-1}; $\sigma(k_{obs.}) = \pm 3.8\%$.

[a] Mole fraction of carbon monoxide in $CO-N_2$ mixture above the reaction solution. [b] Free phosphine removed by reaction with iodine; not used to estimate activation parameters. [c] Uncertainties not corrected for number of degrees of freedom but the estimate of $\sigma(k_{obs.})$ is fully consistent with those found in similar systems.

One reaction of the bisphosphine complex with 0.2 mol dm^{-3} PPh_3 was followed at 170 °C. A slow reaction occurred and i.r. bands at 1 942 and 1 868 cm^{-1} were seen to grow. An e.s.r. spectrum of the solution at room temperature showed a broad band with some evidence for hyperfine splitting. The instrumental noise was rather high and it was not possible to detect all ten fine-structure bands expected for a single unpaired electron in a technetium radical (^{99}Tc has $I = \frac{9}{2}$).

DISCUSSION

Reactions of $[MnRe(CO)_{10}]$ *and* $[MnRe(CO)_3(PPh_3)_2]$.—The substitution of triphenylphosphine into decacarbonylmanganeserhenium has many features in common with substitutions into the dimanganese [8,9] and dirhenium [10] analogues. Thus the rates rise sharply to a limiting value with increasing phosphine concentration, the rise appearing to be more rapid at lower temperatures. The reaction is retarded by carbon monoxide although the same limiting rate is reached at high phosphine concentrations. Thus a plot of $1/k_{obs.}$ against $1/[PPh_3]$ for data at 140 °C is linear with a gradient of 25.7 ± 4.0 mol dm^{-3} s and the inverse of the intercept is $(242 \pm 24) \times 10^{-5}$ s^{-1} in good agreement with the limiting value of $(237 \pm 4) \times 10^{-5}$ s^{-1} found in the absence of carbon monoxide. The reaction proceeds mainly through the mono- to the bis-phosphine complex although some bis complex appears to be formed directly and the mono complex accumulates to a lesser extent the higher the phosphine concentration. The equilibrium constant of 0.8 for the first substitution at 140 °C can be compared with an upper limit of *ca.* 5×10^{-3} for the second substitution estimated by noting the formation of only small amounts of the bis complex with 0.16 mol dm^{-3} under carbon monoxide. Both these equilibria involve the monophosphine isomer in which the phosphine is bound to the rhenium atom.

Over the lower part of the temperature range used the limiting rate of substitution is identical with the limiting rate of reaction with oxygen although the latter is slightly slower at the higher temperatures.[2] The reaction with oxygen has been shown [2] to proceed *via* an initial reversible homolytic fission of the Mn–Re bond, and the identity of the limiting rates of reaction with oxygen and triphenylphosphine at the lower temperatures must be taken as strong evidence for an identity of the rate-determining step. The substitution can therefore be thought to proceed as in equations (1)—(6). However, since the major product of the reaction is the Re–PPh_3 isomer the reaction path represented by equations (1), (3), and (5) must be much more important than that represented by (1), (2), and (4). The indication of some direct formation of the bisphosphine product does suggest, however, that reactions (2) and (6) do occur to some extent. The observation that reaction with phosphine under oxygen still leads to substantial amounts of the monosubstituted complex shows that reactions (3) and (5) must compete successfully with the reactions of the intermediate radicals with oxygen. The absence of any unmixed dimanganese or dirhenium products was also observed in the reaction with oxygen at rates so much below the limiting values that extensive recombination of $[Mn(CO)_5]$ and $[Re(CO)_5]$ radicals must have been occurring.[2] This preference for combination of unlike radicals is also shown in the reaction of $[\{Mn(CO)_4(PPh_3)\}_2]$ with $P(OPh)_3$ where the substitution proceeds *via* homolytic fission to form only $[Mn_2(CO)_8(PPh_3)\{P(OPh)_3\}]$.[3] The relative reactivities of intermediate radicals in these reactions towards substitution, oxidation, and combination with other like or unlike radicals can be inferred from such studies but no clearly defined picture has yet emerged.

$$[(OC)_5MnRe(CO)_5] \rightleftharpoons [Mn(CO)_5] + [Re(CO)_5] \qquad (1)$$

$$[Mn(CO)_5] + PPh_3 \rightleftharpoons [Mn(CO)_4(PPh_3)] + CO \qquad (2)$$

$$[Re(CO)_5] + PPh_3 \rightleftharpoons [Re(CO)_4(PPh_3)] + CO \qquad (3)$$

$$[Mn(CO)_4(PPh_3)] + [Re(CO)_5] \rightleftharpoons [(Ph_3P)(OC)_4MnRe(CO)_5] \qquad (4)$$

$$[Mn(CO)_5] + [Re(CO)_4(PPh_3)] \rightleftharpoons [(OC)_5MnRe(CO)_4(PPh_3)] \qquad (5)$$

$$[Mn(CO)_4(PPh_3)] + [Re(CO)_4(PPh_3)] \rightleftharpoons [(Ph_3P)(OC)_4MnRe(CO)_4(PPh_3)] \qquad (6)$$

The retardation of the reaction by carbon monoxide,

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[9] L. I. B. Haines, D. J. Hopgood, and A. J. Poë, *J. Chem. Soc.* (*A*), 1968, 421.

[10] L. I. B. Haines and A. J. Poë, *J. Chem. Soc.* (*A*), 1969, 2826.

and the concomitant absence of any bisphosphine product at all, is consistent with the reversibility of reactions (2) and (3), (2) being more retarded than (3).

The studies of the reaction of $[MnRe(CO)_8(PPh_3)_2]$ with carbon monoxide were not sufficiently detailed to establish the mechanism conclusively. However, good evidence exists that both $[Mn_2(CO)_8(PPh_3)_2]$ [3] and $[Re_2(CO)_8(PPh_3)_2]$ [1] undergo reversible homolytic fission and it seems unlikely that the mixed-metal complex would react differently.

Reactions of $[Tc_2(CO)_{10}]$ *and* $[Tc_2(CO)_8(PPh_3)_2]$.—Reactions of the decacarbonyl with triphenylphosphine and with oxygen show the same sort of kinetic behaviour as those of the other decacarbonyls. No study was made of the variation, with initial complex concentrations, of initial rates of reaction with oxygen. However, the pronounced decrease with time of the gradients of the first-order rate plots for reaction with low or zero concentrations of oxygen are identical with what has been observed previously [2] and is consistent with an approach to a half-order dependence on $[Tc_2(CO)_{10}]$ as the rates become progressively smaller. Moreover, some data for the dependence of the rates on $[O_2]$ were obtained. These are fully consistent with the mechanism shown in equations (7)—(9), for which the rate equation (10) applies.[2]

$$[Tc_2(CO)_{10}] \rightleftharpoons 2[Tc(CO)_5] \qquad (7)$$

$$[Tc(CO)_5] \longrightarrow \text{decomposition} \qquad (8)$$

$$[Tc(CO)_5] + O_2 \longrightarrow \text{decomposition} \qquad (9)$$

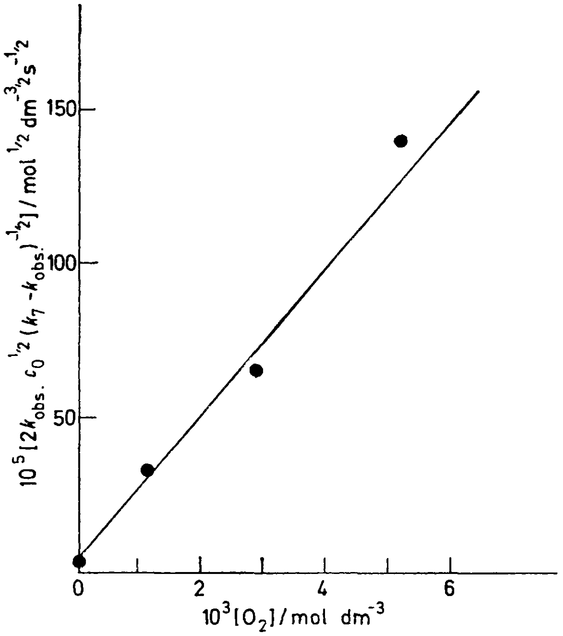
A plot of $2R/(R_7 - R)^{\frac{1}{2}}$ against $[O_2]$ is shown in the

$$2R/(R_7 - R)^{\frac{1}{2}} = (k_8/k_{-7}^{\frac{1}{2}}) + (k_9[O_2]/k_{-7}^{\frac{1}{2}}) \qquad (10)$$

Figure. Values of R were obtained by multiplying the apparent first-order rate constants by the initial concentration of complex. Since the rate of reaction under an atmosphere of pure oxygen at 140 °C is less than the limiting rate of reaction with triphenylphosphine the latter is taken as the value for R_7. A similar procedure was followed for the reaction of $[MnRe(CO)_{10}]$ with oxygen which was also concluded, on the basis of more detailed kinetic data, to proceed by an analogous mechanism to that shown in equations (7)—(9).[2]

Data for reaction of $[Tc_2(CO)_8(PPh_3)_2]$ with carbon monoxide are very limited. It appears to be retarded slightly by the presence of free triphenylphosphine but it seems most probable that the activation parameters obtained are very close to those that would be obtained from limiting rates and that the mechanism, by analogy with reactions of other bisphosphine complexes, involves initial homolytic fission. Supporting evidence is provided by reaction with an excess of PPh_3 which appears to give one or more mononuclear products at a rate much slower than the limiting rate of substitution with carbon monoxide. The i.r. band at 1 942 cm^{-1} can very tentatively be assigned to bis-axial $[Tc(CO)_3(PPh_3)_2]$ since the corresponding rhenium complex absorbs at 1 931 cm^{-1} in decalin.[1,11] The band at 1 868 cm^{-1} could be ascribed to bis-equatorial $[Tc(CO)_3(PPh_3)_2]$ [the analogous 1,2-bis(diphenylphosphino)ethane complex of rhenium has strong bands[12] in benzene at 1 905 and 1 855 cm^{-1}], the higher-energy band expected for this complex being obscured by the band at 1 932 cm^{-1}.

Energetics of the Reactions.—The assignment of homolytic fission mechanisms to the reactions studied here means that the activation enthalpies for the rate-limiting steps can be taken as a kinetic measure of the strengths of the metal–metal bonds. A reasonably good linear correlation of the activation enthalpies for reactions of the four decacarbonyls $[M_2(CO)_{10}]$ (M_2 = Mn_2, Tc_2, Re_2, and MnRe) with the force constants for the M–M stretching vibration has already been shown to exist.[4a] A linear correlation also exists [4a] with the energy of the electronic transition assigned to excitation from the metal–metal σ-bonding orbital to the corresponding antibonding orbital. This assignment was rigorous for $[Mn_2(CO)_{10}]$,[13] and made by analogy for the other decacarbonyls which have generally very similar electronic spectra. This $\sigma \rightarrow \sigma^*$ transition is a measure of the strength of the interaction between the metal atoms. It does not reflect directly any other interactions, steric or electronic, between the two halves of the molecule, and almost certainly overestimates the overall attraction. The gradient of the plot of $\Delta H^{\ddagger}$ against $h\nu(\sigma \rightarrow \sigma^*)$ is only *ca.* 0.3 (when both are measured in the same units) but this can be accounted for to a large degree by this overestimation of the bonding between the two halves of the molecule as measured by $h\nu(\sigma \rightarrow \sigma^*)$. The extent of metal–metal



Dependence of rate of decomposition of decacarbonylditechnetium in decalin at 140 °C on $[O_2]$. $R_7 = k_7c_0$; $R = k_{obs.}c_0$

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[11] F. Nyman, *Chem. and Ind.*, 1965, 604.

[12] M. Freni, D. Giusto, and P. Romiti, *J. Inorg. Nuclear Chem.*, 1967, **29**, 761.

[13] R. A. Levenson, H. B. Gray, and G. P. Ceasar, *J. Amer. Chem. Soc.*, 1970, **92**, 3653.

bond breaking in the transition state can, therefore, be taken to be substantial. The effect of substitution of two phosphine ligands in the axial positions lowers the kinetic strength of the Tc–Tc bond significantly more than it lowers the Mn–Re bond strength. The steric effect of substituents on the kinetic measure of Mn–Mn bond strengths in such carbonyls has been commented on.[4] Thermodynamic data for reversible fission of Fe–Fe bonds in [$\{Fe(C_3H_5)(CO)_2L\}$] also suggest that large substituents L weaken the metal–metal bond although the effect appears to be smaller.[14]

Finally the data in the Figure allow a value of *ca.* 1 × 10^4 dm^3 mol^{-1} at 140 °C to be calculated for k_9/k_8. This is a measure of the relative rates of decomposition of [$Tc(CO)_5$] by oxygen attack and by some spontaneous first-order or pseudo-first-order process. It is comparable with a value of *ca.* 1.4 × 10^4 dm^3 mol^{-1} at 125 °C inferred for the [$Mn(CO)_5$] radical.[2] The gradient of the plot leads to a value of 0.24 $dm^{\frac{3}{2}}$ $mol^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$ for $k_9/k_{-7}^{\frac{1}{2}}$ as compared with 0.54 and 0.42 $dm^{\frac{3}{2}}$ $mol^{-\frac{1}{2}}$ $s^{-\frac{1}{2}}$ for the corresponding dimanganese and manganeserhenium systems at 140 and 155 °C, respectively. The quantitative behaviour of these various radicals involved is, therefore, reasonably independent of the nature of the metal.

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