

Reaction Mechanisms of Metal-metal-bonded Carbonyls. Part 23.¹ Thermal Homolytic Fission of Decacarbonyldirhenium (*Re-Re*)

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The kinetics of thermal decomposition of $[\text{Re}_2(\text{CO})_{10}]$ in decalin under oxygen have been examined. Taken together with data for the substitution reaction with triphenylphosphine the results are qualitatively and quantitatively consistent with initial reversible homolytic fission followed by further reaction of the $[\text{Re}(\text{CO})_5]$ radicals. Activation enthalpies obtained from the data show that $[\text{Re}(\text{CO})_5]$ is considerably more stable than $[\text{Mn}(\text{CO})_5]$. The substitution reaction of $[\text{Re}_2(\text{CO})_{10}]$ with PPh_3 must also occur *via* initial homolytic fission and evidence is presented to suggest that substitution of PPh_3 into $[\text{Re}(\text{CO})_5]$ can be much more rapid than reaction with O_2 and proceeds *via* an associative pathway.

HOMOLYTIC fission of metal-metal bonds in polynuclear transition-metal carbonyls is a process of some interest for several reasons. When accomplished, thermally or photochemically, it produces transition-metal radicals of a type that is relatively rare amongst transition-metal carbonyls.² The physical and chemical study of such reactive radicals has hardly begun, yet it holds out the prospect of discovering new synthetic routes, new types of catalytic reactions, and a better understanding of the bonding in metal carbonyls. Over ten years ago the thermal generation of $[\text{Mn}(\text{CO})_5]$ radicals was cited as a quantitatively satisfactory way of interpreting the results of using $[\text{Mn}_2(\text{CO})_{10}]$ and CCl_4 as co-initiators of vinyl polymerization,³ and the reaction of bromine with $[\text{Mn}_2(\text{CO})_{10}]$ has features characteristic of a long chain reaction propagated by the reactions $[\text{Mn}(\text{CO})_5] + \text{Br}_2 \longrightarrow [\text{Mn}(\text{CO})_5\text{Br}] + \text{Br}$ and $[\text{Mn}_2(\text{CO})_{10}] + \text{Br} \longrightarrow [\text{Mn}(\text{CO})_5\text{Br}] + [\text{Mn}(\text{CO})_5]$.⁴ A chain reaction involving $[\text{Re}(\text{CO})_5]$, $[\text{Re}(\text{CO})_4(\text{PPh}_3)]$, and $[\text{Re}(\text{CO})_3(\text{PPh}_3)_2]$ has recently been implicated in the substitution of PPh_3 into $[\text{Re}(\text{CO})_5\text{H}]$.⁵ No conclusive evidence has yet been obtained for homolytic fission of a single metal-metal bond in a metal carbonyl cluster although a diradical form of $[\text{Ru}(\text{CO})_3(\text{PPh}_3)]$ has been postulated⁶ as a reactive intermediate in the reversible fragmentation of $[\{\text{Ru}(\text{CO})_3(\text{PPh}_3)\}_3]$. Apart from interest in the chemistry of the reactive radicals produced, thermal homolytic fission has a special importance in providing estimates of the strengths of the metal-metal bonds that are more precise and more readily available than those obtained by other methods.⁷

The occurrence of reversible homolytic fission as an initial step in thermal reactions of $[\text{Mn}_2(\text{CO})_{10}]$,⁸ $[\text{MnRe}(\text{CO})_{10}]$,⁸ and $[\text{Tc}_2(\text{CO})_{10}]$,⁹ and of several of their substituted derivatives^{7,10,11} has been conclusively demonstrated by studying the kinetics of thermal decomposition, *etc.* The reversibility of the homolytic-fission step ensures that the rates of reaction decrease below that of rate-limiting homolytic fission when further reaction of the $[\text{M}(\text{CO})_5]$ or $[\text{M}(\text{CO})_4\text{L}]$ radicals produced does not compete successfully with radical recombination. This competition can be controlled by varying the concentration of complex or of reagents that react with the radical, *e.g.* O_2 , $\text{C}_2\text{H}_2\text{Cl}_4$, *etc.* In addition to the decrease

in rate resulting from radical recombination, the second-order nature of the recombination leads to a decrease below unity of the order of the reaction with respect to [complex]. When recombination is much faster than further reaction the rates become half-order in [complex]. Reversible homolytic fission therefore shows several distinctive features that allow it to be readily detected by kinetic studies and we report here kinetic data for the thermal reaction of $[\text{Re}_2(\text{CO})_{10}]$ with O_2 in decalin. In conjunction with results for the substitution reaction with triphenylphosphine, they conform qualitatively and quantitatively with those expected when reversible homolytic fission is the initial step.

EXPERIMENTAL AND RESULTS

The compound $[\text{Re}_2(\text{CO})_{10}]$ (Strem Chemicals, Inc.) was found to be spectroscopically pure and was used as received. All other reagents and procedures were identical with those described previously.^{8,9} When the concentration of complex was high the final product of the decomposition reaction with oxygen was a black precipitate, presumably of rhenium oxide. This was filtered off before spectroscopic analysis of the solutions. Reactions of more dilute solutions did not lead to precipitates and filtration was not necessary. Reactions were followed by monitoring the decreasing absorbance, A , due to $[\text{Re}_2(\text{CO})_{10}]$ either in the i.r. at $2\,070\text{ cm}^{-1}$ or in the near u.v. at 311 nm . For reactions with O_2 absorbance decreased to zero, no C-O stretching bands characteristic of terminally co-ordinated CO being evident in the i.r. A broad band at *ca.* $1\,720\text{ cm}^{-1}$ was also observed to grow and is assigned to uncharacterized products of solvent oxidation, similar bands having been seen^{8,9} in corresponding reactions of $[\text{Mn}_2(\text{CO})_{10}]$, $[\text{MnRe}(\text{CO})_{10}]$, and $[\text{Tc}_2(\text{CO})_{10}]$. The data were plotted as for simple first-order reactions although the rate plots tended to curve downwards with time to an extent increasing with increasing initial concentration, c_0 , of complex and decreasing $[\text{O}_2]$. Apparent first-order rate constants were then obtained from the initial slopes of such plots which were reasonably linear for at least one half-life. Decomposition in the presence of smaller concentrations of O_2 and at higher temperatures gave quite good linear plots of $A^{\frac{1}{2}}$ against time. However, relatively few of the plots were of this extreme kind and, for consistency, all the data were obtained as apparent first-order rate constants. Reactions under Ar at 180°C led to some black precipitate but also to a soluble carbonyl-containing species showing C-O stretching frequencies at

2 034m and 1 931s(br) cm^{-1} that remained quite steady even after all the $[\text{Re}_2(\text{CO})_{10}]$ had reacted. The kinetics of these reactions were not at all reproducible, however. The presence of CO reduced the rates greatly and no carbonyl-containing product was observed.

Reaction with PPh_3 followed a similar course to that already described.¹² The i.r. spectra changed in a way consistent with the formation^{12,13} of $[\text{Re}_2(\text{CO})_9(\text{PPh}_3)]$ and $[\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2]$, the latter being the only product observed at the end of the reaction. Reactions were followed by monitoring the i.r. band at 2 070 cm^{-1} due to $[\text{Re}_2(\text{CO})_{10}]$. No spectroscopic evidence was seen of the many other products reported after reaction of $[\text{Re}_2(\text{CO})_{10}]$ and PPh_3 in xylene at reflux temperatures for 48 h.¹⁴ Thermal reaction of $[\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2]$ with PPh_3 in decalin is much slower than the preceding substitutions.¹³ One reaction with 0.08 mol dm^{-3} PPh_3 was performed at 160 °C under an atmosphere of pure O_2 . No change in the nature of the products or of the rate of reaction was observed. Rate data for reactions with O_2 and PPh_3 are given in Tables 1 and 2.

TABLE 1

Temperature dependence of reactions of $[\text{Re}_2(\text{CO})_{10}]$ with O_2 and PPh_3 in decalin. $c_0^a = 4 \times 10^{-4}$ mol dm^{-3}

$\theta_c/\text{°C}$	$10^5 k(\text{PPh}_3) \text{ } ^b/\text{s}^{-1}$	$10^5 k(\text{O}_2) \text{ } ^c/\text{s}^{-1}$
120.2	0.236, 0.234	0.252, 0.242
130.0	0.831, 0.866	0.920, 0.917
140.0	3.06, 2.95	2.99
150.0	9.95, 9.79	8.96, 9.02
160.0	29.6, 30.0	18.1, 18.3, 17.2
170.0	83.2, 84.8	37.2, 44.0
180.0	220, 218	105
	217, ^d 220	

^a Initial concentration of complex. ^b $[\text{PPh}_3] = 0.09$ mol dm^{-3} except where indicated. ^c Apparent first-order rate constants from initial slopes of first-order rate plots for reaction under pure O_2 . ^d $[\text{PPh}_3] = 0.20$ mol dm^{-3} .

DISCUSSION

The results in Table 1 show that apparent first-order rate constants for decomposition under O_2 at 120 and 130 °C are essentially the same as those for substitution by PPh_3 . Excellent first-order rate plots were obtained over > 80% completion of the reaction. However, as the reaction temperature increases the rate constants for decomposition become progressively smaller compared with those for substitution. The first-order rate plots for substitution remain excellently linear but those for decomposition become progressively more curved, gradients increasing with time. At 180 °C the apparent first-order rate constant from the initial gradient is only ca. 50% of that for substitution. The more extensive data in Table 2 show that the apparent first-order rate constants for decomposition decrease monotonically by as much as a factor of five with increasing initial concentration, c_0 , of complex. At a constant c_0 the rate constants increase with $[\text{O}_2]$.

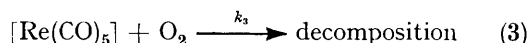
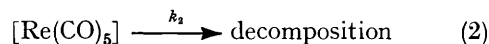
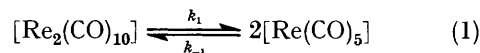
This behaviour parallels that shown^{8,9} by decomposition of $[\text{Mn}_2(\text{CO})_{10}]$, $[\text{MnRe}(\text{CO})_{10}]$, and $[\text{Tc}_2(\text{CO})_{10}]$ and the mechanism shown in equations (1)–(3) can, therefore, be proposed. The rate equation for this mechanism can be written as in (4) or (5) where $a = (k_2 + k_3 - [\text{O}_2])/k_{-1}$. If the values of k_{obs} are not too much below k_1

TABLE 2
Rate data for thermal reaction of $[\text{Re}_2(\text{CO})_{10}]$ with O_2 in decalin

$\theta_c/\text{°C}$	$10^5 c_0$	$10^4 [\text{O}_2]^a$ mol dm^{-3}	$10^4 k_{\text{obs}} \text{ } ^b$ s^{-1}	$10^4 a \text{ } ^c$ $\text{mol}^{1/2} \text{dm}^{-3/2} \text{s}^{-1}$
159.3	5.96	1.93 ^d	1.21	1.40
	36.7		0.564	1.40
	60.6		0.396	1.30
	7.50	7.64 ^e	1.41	1.96
	12.0		1.17	1.90
	13.1		1.07	1.80
	21.8		1.21	2.67
	23.0		0.826	1.72
	36.0		0.778	2.02
	51.2		0.869	2.72
	77.2		0.683	2.52
	93.2		0.633	2.54
	210		0.376	2.13
	310		0.282	1.90
	402		0.271	2.08
	587		0.271	2.52
	148	20.5 ^f	1.08	5.96
	180		0.917	5.42
	246		0.781	5.26
	120	36.4 ^g	1.62	9.66
207		1.15	7.82	
210		1.19	8.20	
169.2	92.6	5.69 ^e	1.33	3.04
	133		1.29	3.50
	90.1	15.3 ^f	2.36	5.80
	135		1.90	5.48
	143	27.1 ^g	2.99	9.72
	286		2.06	8.72
	467		1.61	8.44
	697		1.13	7.02
	712		1.30	8.20
	956		1.24	9.12
179.0	974		1.06	7.72
	31.4	3.30 ^e	4.52	3.84
	33.2		3.89	3.32
	45.2		3.01	2.94
	65.6		3.25	3.84
	25.5	8.80 ^f	6.75	5.52
	34.8		6.47	6.00
	65.2		4.63	5.68
	7.5	15.7 ^g	14.5	9.20
	31.7		7.87	7.48
34.5		9.28	9.60	

^a Estimated as described in ref. 8. ^b Apparent first-order rate constants from initial slopes of first-order rate plots. ^c $a = 2k_{\text{obs}}c_0^{\frac{1}{2}}(k_1 - k_{\text{obs}})^{-\frac{1}{2}}$; k_1 = limiting rate constant for substitution reaction with PPh_3 . ^d Reaction under 5.3 mol % O_2 in O_2 - N_2 mixture. ^e Reaction under air. ^f Reaction under 56.3 mol % O_2 . ^g Reaction under pure O_2 .

then equation (4) can be used¹⁰ to obtain k_1 independently from the intercept of a plot of k_{obs} against $k_{\text{obs}}^2 c_0$ at constant $[\text{O}_2]$. In the reactions studied here over a wide range of c_0 the maximum value of k_{obs} is less than ca. 50%



$$k_{\text{obs}} = k_1 - (4k_{\text{obs}}^2 c_0 / a^2) \quad (4)$$

$$2k_{\text{obs}} c_0^{\frac{1}{2}} / (k_1 - k_{\text{obs}})^{\frac{1}{2}} = a \quad (5)$$

of the value expected for k_1 from the limiting rate constant for substitution. The extrapolation to $k_{\text{obs}}^2 c_0 = 0$ is, therefore, too long to give precise values of k_1 . We,

therefore, assume them to be given by the limiting rate constant for substitution. This procedure was followed in analyzing similar data for $[\text{MnRe}(\text{CO})_{10}]$ ⁸ and $[\text{Tc}_2(\text{CO})_{10}]$ ⁹. It is justified by the identity of the rates of substitution and decomposition at lower temperatures which strongly suggests that both reactions are going by

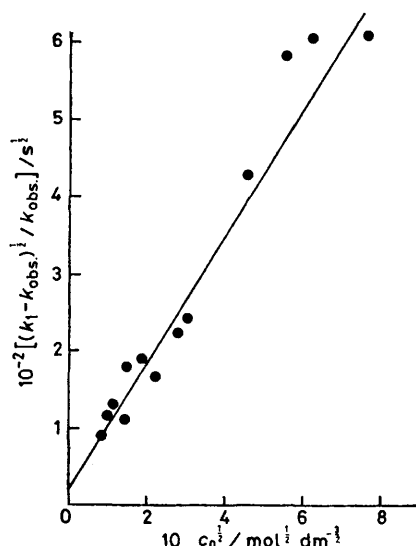


FIGURE 1 Dependence of apparent first-order rate constants, $k_{\text{obs.}}$, for decomposition of $[\text{Re}_2(\text{CO})_{10}]$ in decalin under air on concentration of $[\text{Re}_2(\text{CO})_{10}]$. k_1 = limiting rate constant at high $[\text{O}_2]$ and/or low [complex]

the same rate-determining steps. Equation (5) can therefore be used as a test of the fit of the data to the proposed mechanism. At constant $[\text{O}_2]$ a plot of $(k_1 - k_{\text{obs.}})^{1/2}/k_{\text{obs.}}$ against $c_0^{1/2}$ should be linear and should pass through the origin. The data for reaction under air at 159.3 °C ($[\text{O}_2] = 3.64 \times 10^{-4} \text{ mol dm}^{-3}$) are plotted in this way in Figure 1. The straight line is a least-squares plot for which the intercept is not assumed to be zero. Each value of $(k_1 - k_{\text{obs.}})^{1/2}/k_{\text{obs.}}$ is assumed to have a constant percent uncertainty. This is roughly equivalent to assuming $k_{\text{obs.}}$ to have a constant percent uncertainty since $k_{\text{obs.}}$ is generally much less than k_1 and the power of $\frac{1}{2}$ in the denominator minimizes the contribution of this term to the overall uncertainty. The intercept is $(0.19 \pm 0.15) \times 10^2 \text{ s}^{\frac{1}{2}}$, *i.e.* not distinguishably different from zero, and $\sigma(k_{\text{obs.}}) = 17.5\%$. A similar analysis of the data for reaction under pure O_2 at 169.2 °C ($[\text{O}_2] = 2.71 \times 10^{-3} \text{ mol dm}^{-3}$) gave an intercept of $(-0.26 \pm 0.17) \times 10^2 \text{ s}^{\frac{1}{2}}$ and $\sigma(k_{\text{obs.}}) = 11.4\%$. In all cases the uncertainties are estimates of the standard deviations adjusted for the number of degrees of freedom so that 95% confidence levels can be obtained by doubling the uncertainties.

The conformity to the mechanism of the $[\text{O}_2]$ dependence of the rates can be examined by plotting a against $[\text{O}_2]$. Values of a are given in Table 2 and a plot of the data at 159.3 °C is shown in Figure 2 to be linear, as expected. A linear least-squares analysis of the data leads to the values of $k_2/k_{-1}^{\frac{1}{2}}$ and $k_3/k_{-1}^{\frac{1}{2}}$ shown in Table 3. Each value of a (and, therefore, of $k_{\text{obs.}}$, see above) was

TABLE 3

Rate parameters obtained by analysis of data according to the reversible homolytic fission mechanism

θ_c °C	$10^6 k_2/k_{-1}^{\frac{1}{2}}$ $\text{mol}^{\frac{1}{2}} \text{dm}^{-\frac{3}{2}} \text{s}^{-\frac{1}{2}}$	$10 k_3/k_{-1}^{\frac{1}{2}}$ $\text{dm}^{\frac{3}{2}} \text{mol}^{-\frac{1}{2}} \text{s}^{-\frac{1}{2}}$	$10^{-3} k_3/k_2$ $\text{dm}^3 \text{mol}^{-1}$	$\sigma(a)^*$ %
159.3	7.90 ± 1.38	1.90 ± 0.20	2.5 ± 0.7	17.3
169.2	19.2 ± 3.3	2.35 ± 0.20	1.3 ± 0.3	10.9
179.0	20.2 ± 3.1	4.17 ± 0.47	2.2 ± 0.6	12.3
	$\Delta H_2^{\ddagger} - 0.5 \Delta H_{-1}^{\ddagger} = 75 \pm 40 \text{ kJ mol}^{-1}$			
	$\Delta S_2^{\ddagger} - 0.5 \Delta S_{-1}^{\ddagger} = -25 \pm 90 \text{ J K}^{-1} \text{ mol}^{-1}$			
	$\Delta H_3^{\ddagger} - 0.5 \Delta H_{-1}^{\ddagger} = 63 \pm 17 \text{ kJ mol}^{-1}$			
	$\Delta S_3^{\ddagger} - 0.5 \Delta S_{-1}^{\ddagger} = 10 \pm 45 \text{ J K}^{-1} \text{ mol}^{-1}$			

* An approximate measure of $\sigma(k_{\text{obs.}})$; see text.

assumed to have the same percent uncertainty. In view of the fact that the values of $k_{\text{obs.}}$ are based on initial-rate measurements over an 80-fold range of c_0 and a 20-fold range of $[\text{O}_2]$, these data must be considered to be in excellent agreement with the proposed mechanism. The alternatives of heterolytic fission into $[\text{Re}(\text{CO})_5]^+$ and $[\text{Re}(\text{CO})_5]^-$ or unsymmetrical fission into $[\text{Re}(\text{CO})_6]$ and $[\text{Re}(\text{CO})_4]$ cannot be excluded on purely kinetic grounds. The former can, however, be rejected⁸ because the two ions would be strongly ion-paired in decalin and the reverse of the fission process would be a unimolecular reaction of the ion pair. No dependence of $k_{\text{obs.}}$ on [complex] would then be observed. The latter can be rejected⁸ on energetic grounds.

Any significant contribution from a heterogeneous pathway can also be rejected. Addition of freshly precipitated oxide product had no effect on the corresponding reactions of $[\text{Mn}_2(\text{CO})_{10}]$ ⁸ and the decrease in rate and order of reaction below the expected limiting

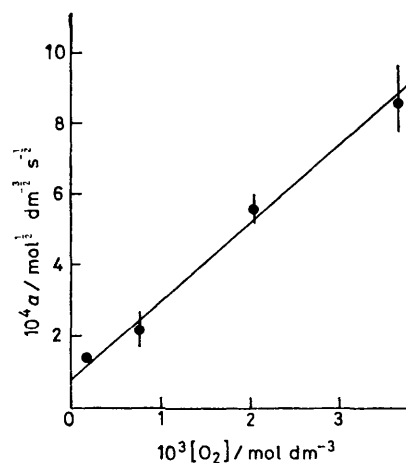


FIGURE 2 Dependence on $[\text{O}_2]$ of apparent first-order rate constants, $k_{\text{obs.}}$, for decomposition of $[\text{Re}_2(\text{CO})_{10}]$ in decalin. $a = 2k_{\text{obs.}}c_0^{1/2}/(k_1 - k_{\text{obs.}})^{\frac{1}{2}}$; k_1 = limiting rate constant at high $[\text{O}_2]$ and/or low [complex]. The points refer to the average values of a and the error bars show the range of values of a

values was pronounced even for those reactions in which no trace of precipitate was observed. In any case it is hard to see how the presence of an oxide precipitate could actually retard a reaction. Reversible homolytic fission is, therefore, the only reasonable mechanism in accordance with the data.

The participation of intermediate hydrido-complexes in such reactions may be important. Brown and co-workers² showed that substituted $[\text{Mn}(\text{CO})_5]$ radicals can abstract hydrogen atoms from hydrocarbon solvents and it seems highly likely that $[\text{Re}(\text{CO})_5]$ can do the same. (Reaction with H_2 itself certainly occurs.¹⁵) Formation of $[\text{Re}(\text{CO})_5\text{H}]$ in this way could account for the $[\text{O}_2]$ -independent pathway for decomposition and for the latter's irreproducibility in the absence of O_2 . Thus, the rate of formation of $[\text{Re}(\text{CO})_5\text{H}]$ could be the rate-limiting step for this path, subsequent decomposition in the presence of O_2 being rapid. If no O_2 is present the $[\text{Re}(\text{CO})_5\text{H}]$ could react to form higher hydridocarbonyl clusters by paths involving⁵ $[\text{Re}(\text{CO})_5]$ in rate-determining steps so that the simple rate equations derived for our proposed mechanism would be completely inappropriate. The appearance of bands at *ca.* $1\,700\text{ cm}^{-1}$ during reaction with O_2 could also be explained by oxidation of those solvent molecules from which hydrogen atoms have been abstracted.

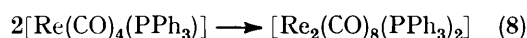
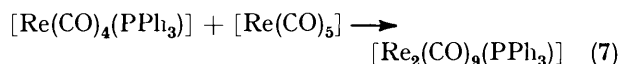
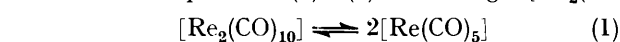
The direct reaction of $[\text{Re}(\text{CO})_5]$ with O_2 is first order in $[\text{O}_2]$ over the concentration range used. It seems likely that O_2 should react very rapidly with $[\text{Re}(\text{CO})_5]$ to form $[\text{Re}(\text{CO})_5(\text{O}_2)]$ but that this adduct is relatively stable.⁵ If this is so the first-order dependence on $[\text{O}_2]$ must arise from a rapid pre-equilibration of $[\text{Re}(\text{CO})_5(\text{O}_2)]$ and $[\text{Re}(\text{CO})_5]$, the concentration of the former being relatively small. At high enough concentrations of O_2 the rate should become independent of $[\text{O}_2]$.

Reversible dissociation of CO from $[\text{Re}(\text{CO})_5]$, $[\text{Re}(\text{CO})_5\text{H}]$, and $[\text{Re}(\text{CO})_5(\text{O}_2)]$ is probably involved in these reactions. Decomposition of $[\text{Re}_2(\text{CO})_{10}]$ {and $[\text{Tc}_2(\text{CO})_{10}]$ ⁹} is strongly retarded by CO in contrast to that of $[\text{Mn}_2(\text{CO})_{10}]$ ⁸ where CO-dissociative steps only become detectable at higher temperatures. This difference in behaviour of $[\text{Mn}_2(\text{CO})_{10}]$ and $[\text{Re}_2(\text{CO})_{10}]$ may be reflected in the different values of the activation parameters. The value⁸ of -28 kJ mol^{-1} for $\Delta H_2^\ddagger - 0.5\Delta H_{-1}^\ddagger$ for $[\text{Mn}_2(\text{CO})_{10}]$ is surprising. It is, however, quite precise because it is based on values of $\Delta H_2^\ddagger - 0.5(\Delta H_{-1}^\ddagger - \Delta H_1^\ddagger)$ and ΔH_1^\ddagger obtained over a $100\text{ }^\circ\text{C}$ range. It was originally suggested⁸ (on the basis of the kinetic parameters combined with mass spectrometric measurements¹⁵ of the homolytic fission equilibrium in the gas phase) that ΔH_{-1}^\ddagger was *ca.* 50 kJ mol^{-1} so that ΔH_2^\ddagger was *ca.* 0 kJ mol^{-1} . However, ΔH_{-1}^\ddagger has since been shown by more direct, kinetic studies¹⁶ to be itself *ca.* 0 kJ mol^{-1} so that ΔH_2^\ddagger is quite pronouncedly negative. The implications of this are not at all clear. The value of $\Delta H_2^\ddagger - 0.5\Delta H_{-1}^\ddagger$ for $[\text{Re}_2(\text{CO})_{10}]$ is only very approximate because it is based on the temperature dependence (over only $20\text{ }^\circ\text{C}$) of the intercepts of plots like that in Figure 2. These intercepts are themselves rather approximate (Table 3). In spite of its imprecision the value is at least consistent with a more straightforward, higher energy path for decomposition of $[\text{Re}(\text{CO})_5]$ by H abstraction and/or CO dissociation. The value of $\Delta H_3^\ddagger - 0.5\Delta H_{-1}^\ddagger$ for $[\text{Re}_2(\text{CO})_{10}]$ is also considerably higher than that (*ca.* $8 \pm 10\text{ kJ mol}^{-1}$)⁸

for $[\text{Mn}_2(\text{CO})_{10}]$, again indicating a greater stability for $[\text{Re}(\text{CO})_5]$ compared with $[\text{Mn}(\text{CO})_5]$. The value ($14 \pm 12\text{ kJ mol}^{-1}$) for $[\text{Tc}_2(\text{CO})_{10}]$ ¹⁷ is closer to that for $[\text{Mn}_2(\text{CO})_{10}]$ than for $[\text{Re}_2(\text{CO})_{10}]$.

No explicit consideration has been given to the existence during the reaction of radical pairs trapped in a solvent cage. Provided the radicals do not decompose, either spontaneously or by reaction with O_2 , before they separate from each other, then the rate equations are quite unaffected. If direct decomposition of the radicals in the solvent cage did occur, then the order of the reaction with respect to complex concentration would never quite reach 0.5. The linearity of the plot in Figure 1 suggests that it does and the data⁸ for decomposition of $[\text{Mn}_2(\text{CO})_{10}]$ under argon or CO show clearly that it does in that case. The dissociation of any radical pairs present must therefore be much faster than the rates of any competing reactions.

The identity of the rates of reaction of $[\text{Re}_2(\text{CO})_{10}]$ with O_2 and PPh_3 at the lower temperatures shows that substitution must also be occurring *via* initial homolytic fission. This is followed by substitution into the 17-electron radical, $[\text{Re}(\text{CO})_5]$, and recombination of radicals to form $[\text{Re}_2(\text{CO})_9(\text{PPh}_3)]$ and $[\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2]$ as shown in equations (6)–(8). Although $[\text{Re}_2(\text{CO})_9(\text{PPh}_3)]$ is observed as a product, $[\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2]$ is also formed as a direct product¹² in conformity with this mechanism. The ratio of di- to mono-substituted product increases with increasing $[\text{PPh}_3]$. The retardation by CO of reactions¹² at lower $[\text{PPh}_3]$ is indicative of the ready reversal of reaction (6), a step that is also required in the reaction of $[\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2]$ with CO to form $[\text{Re}_2(\text{CO})_9(\text{PPh}_3)]$.¹³ An important observation is that the reaction of $[\text{Re}_2(\text{CO})_{10}]$ with 0.08 mol dm^{-3} PPh_3 still leads to formation of $[\text{Re}_2(\text{CO})_9(\text{PPh}_3)]$ and $[\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2]$ in high yields at $160\text{ }^\circ\text{C}$, even when the reaction is carried out under an atmosphere of O_2 . This shows that the rate of reaction of $[\text{Re}(\text{CO})_5]$ with 0.08 mol dm^{-3} PPh_3 is much faster than that with $3.6 \times 10^{-3}\text{ mol dm}^{-3}$ O_2 and that the rate of reaction of $[\text{Re}(\text{CO})_4(\text{PPh}_3)]$ with O_2 at $c_0 = 4 \times 10^{-4}\text{ mol dm}^{-3}$ is less than its rate of reaction either with $[\text{Re}(\text{CO})_5]$ or with another $[\text{Re}(\text{CO})_4(\text{PPh}_3)]$ radical.



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Since the rate of reaction of $[\text{Re}(\text{CO})_5]$ with PPh_3 can be so much faster than with O_2 , it must also be very much faster than its rate of decomposition by the path shown in (2). This makes it most probable that reaction with PPh_3 is first order in $[\text{PPh}_3]$, *i.e.* the substitution is $\text{S}_{\text{N}}2$ or associative. If the substitution were in fact dissociative then CO dissociation from $[\text{Re}(\text{CO})_5]$ would be very rapid compared with the first-order or pseudo-first-order reaction (2). The dissociation would also have to

be completely reversible (even under O₂ or under Ar in the absence of added free CO) or it would presumably provide a path for much more rapid decomposition of [Re(CO)₅] than is actually observed. Kidd and Brown² have argued in favour of a dissociative mechanism mainly because they considered the associative path would be too slow. They concede, however, that they are equally unable to account for why the dissociative process should be so rapid. Detailed kinetic studies have shown¹¹ that displacement of PPh₃ from [Mn(CO)₄(PPh₃)] by P(OPh)₃ must occur *via* an associative pathway and there seems no reason why this should not also be the case for reaction (6). More extensive studies of this sort are required to establish the generality of such a mechanism.

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