Reaction Mechanisms of Metal–Metal-bonded Carbonyls. Part 16.[1] Reversible Fragmentation of *cyclo*-Tris[tricarbonyl(triphenylphosphine)-ruthenium] (3 *Ru–Ru*)

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The kinetics of reaction in decalin of $[\{Ru(CO)_3(PPh_3)\}_3]$ with oxygen in the presence of triphenylphosphine have been studied and shown to involve reversible fragmentation into two species, only one of which reacts directly with oxygen. It is suggested that the two species are $[\{Ru(CO)_3(PPh_3)\}_2]$ and high-spin tetrahedral $[Ru(CO)_3(PPh_3)]$. Kinetic parameters for the fragmentation process are $k(100\ °C) = 1.1 \times 10^{-2}\ s^{-1}$, $\Delta H^{\ddagger} = 130.0 \pm 2.5$ kJ mol^{-1}, and $\Delta S^{\ddagger} = 64.2 \pm 7.5$ J K^{-1} mol^{-1}. The immediate products of the reaction are triphenylphosphine oxide and an insoluble, involatile, yellow ruthenium complex that has not yet been characterized. When generated at low concentrations in toluene, the yellow complex changes to a green one that catalytically oxidizes PPh_3.

Reversible, thermal, homolytic fission of the metal–metal bonds in $[Mn_2(CO)_{10}]$,[2] $[MnRe(CO)_{10}]$,[2] $[Tc_2(CO)_{10}]$,[3] $[Re_2(CO)_{10}]$,[4] and $[Mn_2(CO)_8(PPh_3)_2]$ [5] has recently been demonstrated kinetically. Activation enthalpies for the fission process provide a useful measure of the strengths of the metal–metal bonds. We are extending these studies to include fragmentation reactions of *triangulo* metal clusters of the type $[\{Ru(CO)_3L\}_3]$ and have recently reported [6] activation parameters that we have assigned to reaction (i) which occurs as the primary

$$[\{Ru(CO)_3(PPh_3)\}_3] \longrightarrow [\{Ru(CO)_3(PPh_3)\}_2] + [Ru(CO)_3(PPh_3)] \qquad \text{(i)}$$

step in the reaction with triphenylphosphine under an atmosphere of carbon monoxide to form $[Ru(CO)_3(PPh_3)_2]$. This reaction is first order in the concentration of $[\{Ru(CO)_3(PPh_3)\}_3]$ and is therefore irreversible under the conditions used. We report here some kinetic studies of the reaction of $[\{Ru(CO)_3(PPh_3)\}_3]$ with oxygen, in the presence of PPh_3, that provide clear evidence that this complex can react by a kinetically quite distinct path that involves initial *reversible* fragmentation.

EXPERIMENTAL AND RESULTS

The chemicals used, and the procedures followed in carrying out the kinetics, were the same as those described previously.[6]

Course of the Reaction.—Reaction of oxygen with $[\{Ru(CO)_3(PPh_3)\}_3]$ in decalin in the presence of only trace amounts of triphenylphosphine is preceded by an ill defined induction period after which a black-brown precipitate is formed. In the presence of substantial concentrations of free PPh_3, however, the reaction proceeds smoothly between 55 and 75 °C with formation of a yellow ruthenium-containing precipitate from which triphenylphosphine oxide could be isolated by extraction with methanol and characterized by means of its i.r. spectrum. The yellow product was insoluble in most solvents but dissolved very sparingly in benzene from which it was recrystallized. Thin-layer chromatography on silica failed to effect any separation of the product. Analysis for C, H, P, and Ru, mass-spectrometric analysis, and i.r. spectroscopy failed to provide any clear evidence of the nature of the compound although the last did show the presence of a strong band at 1 662 cm^{-1} that might be attributable to a carbonato-ligand. The complex $[\{Ru(CO)_3(PPh_3)\}_3]$ does react with oxygen in the solid state to form a species containing such a ligand.[7]

When the reaction was carried out in toluene at 100 °C the yellow compound did not precipitate until [complex] $\geqslant 5 \times 10^{-4}$ mol dm^{-3}. A quantitative estimate of the amount of PPh_3O formed was made by measuring the intensity of the P–O stretching band at 1 200 cm^{-1} and showed that 1 mol of PPh_3 was oxidized for every mol of ruthenium that reacted to form the yellow product. On continued heating of the yellow solution for *ca.* 1 h it turned green, and in *ca.* 5 h the green solution catalytically oxidized *ca.* 20 mol of PPh_3 per mol of Ru in solution.

Kinetics of the Reaction.—The kinetics were followed by monitoring the intensity of the i.r. band [6] at 1 975 cm^{-1} due to the complex $[\{Ru(CO)_3(PPh_3)\}_3]$, or by following the decreasing intensity of the u.v.-visible band at 510 nm. In both cases the intensity decreased to zero, the yellow product appearing as a dense precipitate in the bottom of the reaction vessel. First-order rate plots generally showed marked curvature, the gradients increasing with time, but half-order rate plots were more linear. Separation of the precipitate by filtration before monitoring the samples did not affect the rate plots. Since the order of the reaction was in doubt all the kinetic data were expressed as initial rates, R_0, obtained by multiplying the initial concentrations, c_0, by the *apparent* first-order rate constants measured by the initial gradient of first-order plots. Rates were found to increase sharply with $[PPh_3]$ and reached limiting values at $[PPh_3] \geqslant 0.05$ mol dm^{-3}. Most data were obtained with $[PPh_3] = 0.2$ mol dm^{-3} and these are reported in Table 1.

DISCUSSION

Although the detailed natures of the yellow and green products are not known the kinetic data are susceptible to detailed interpretation as follows.

The plots of log R_0 against log c_0 (Figure 1) show that the order of the reaction with respect to the concentration of $[\{Ru(CO)_3(PPh_3)\}_3]$ decreases below unity as the concentration of complex increases and/or as $[O_2]$ decreases. This is an immediate and unambiguous

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[1] Part 15, J. P. Fawcett and A. J. Poë, *J.C.S. Dalton*, 1977, 1302.

[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] A. J. Poë and K. R. Sharma, unpublished work.

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

[6] D. P. Keeton, S. K. Malik, and A. J. Poë, *J.C.S. Dalton*, 1977, 233.

[7] J. Valentine, D. Valentine, and J. P. Collman, *Inorg. Chem.*, 1971, **10**, 219.

TABLE 1

Initial rates of reaction of $[\{Ru(CO)_3(PPh_3)\}_3]$ with oxygen in decalin. $[PPh_3] = 0.2$ mol dm^{-3}

θ_c / °C	10^5c_0 / mol dm^{-3}	$10^4[O_2]$[a] / mol dm^{-3}	$10^{10}R_0$ / mol dm^{-3} s^{-1}	$10^{10}R_0$(calc.)[b] / mol dm^{-3} s^{-1}	$100[R_0(\text{calc.}) - R_0]/R_0(\text{calc.})$
74.6	87.4	3.8	196	204	−3.9
	19.1	3.8	81	93	+12.9
	8.98	3.8	71	62	−14.5
	6.66	3.8	52	53	+1.9
	6.40	3.8	64	52	−22.1
	4.44	3.8	38	42	+9.9
	2.20	3.8	28	29	+1.4
	1.60	3.8	26	24	−8.9
	0.64	3.8	11	14	+21.2
	96.9	15.0	479	419	−12.2
	55.7	15.0	295	313	+5.8
	50.8	15.0	221	298	+25.8
	50.6	15.0	206	297	+30.6
	20.3	15.0	205	182	−12.6
	8.88	15.0	126	117	−7.2
	7.77	15.0	107	106	−0.9
	6.66	15.0	92	97	+5.2
	5.34	15.0	94	85	−10.6
	5.0	15.0	89	82	−8.9
	53.7	40	500	484	−3.3
	51.2	40	496	471	−5.3
	50.9	40	429	470	+8.7
	115	71	1 460	1 201	−21.6
	52.7	71	692	771	+10.2
	52.1	71	657	765	+14.2
	51.7	71	863	762	−13.3
	51.1	71	622	757	+17.8
	51.1	71	669	757	+11.6
	50.9	71	766	752	−1.8
	40.0	71	662	655	−1.1
	38.0	71	609	635	+4.2
	19.0	71	509	415	−22.6
	8.88	71	267	251	−6.4
	7.77	71	237	229	−3.6
	6.67	71	216	205	−5.2
	5.60	71	187	181	−3.2
	5.10	71	179	169	−5.9
	4.40	71	154	152	−1.7
	3.30	71	124	120	−3.3
	2.22	71	89	88	−1.5
	1.32	71	57	57	0
	1.32	71	59	57	−2.6
	0.95	71	44	43	−2.4
	0.64	71	31	31	0
	0.67	71	32	31	−3.3
72.2	8.88	71	180		
	7.77	71	165		
	6.67	71	147		
	5.34	71	130		
	4.80	71	108		
	3.33	71	79		
	2.22	71	62		
	0.95	71	30		
65.0	8.88	72	71		
	7.77	72	67		
	6.66	72	61		
	4.44	72	45		
	3.33	72	35		
	2.22	72	24.8		
	1.11	72	13.5		
54.9	8.88	73	21.5		
	6.66	73	17.1		
	5.55	73	14.4		
	4.44	73	11.9		
	3.24	73	9.0		
	2.22	73	6.4		
	1.13	73	3.4		

[a] Derived from measurements in M. Basato, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, 1974, 1350. [b] Calculated as described in the Discussion section.

qualitative indication that the complex undergoes initial reversible fission into two or more fragments and that one or more of the fragments reacts directly with oxygen. The results also indicate that the deviation from first-order behaviour cannot be caused by the presence of precipitate. Thus, at low values of c_0 the reaction changes from being close to half-order in [complex] at low $[O_2]$ to close to first order at high $[O_2]$ even though the amount of precipitate formed was approximately the same in both sets of runs. The linearity of the half-order rate plots at low $[O_2]$ shows that the half-order rate constants are indeed constant for up to 75% completion of reaction even though no precipitate is present initially and a detectable amount is present at 75% reaction. This is true for values of c_0 covering a range of $\geqslant$ *ca.* 100 so that the amount of precipitate formed varies enormously without affecting the rate constants. Finally, the excellent fit of the data, over the wide ranges of c_0 and $[O_2]$ used, to a particular mechanism (see below) makes it virtually impossible for the reaction to be heterogeneous. The three most obviously possible mechanisms are shown in equations (1)—(7). The species $[Ru_3L_3]$, $[Ru_2L_2]$, and [RuL] symbolize the complexes $[\{Ru(CO)_3(PPh_3)\}_3]$, $[\{Ru(CO)_3(PPh_3)\}_2]$, and $[Ru(CO)_3(PPh_3)]$, respectively. Mechanisms (IIIa) and (IIIb) differ only in which of the two fragments formed in the initial fission process reacts directly with oxygen, and they are kinetically indistinguishable.

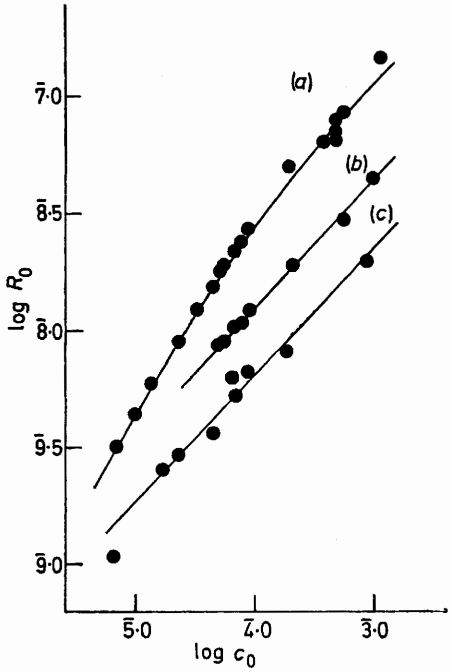

FIGURE 1 Dependence of initial rates of decomposition of $[\{Ru(CO)_3(PPh_3)\}_3]$ in decalin under O_2–N_2 mixtures at 74.6 °C. $[PPh_3] = 0.2$ mol dm^{-3}. (*a*) 100% O_2 (7.1×10^{-3} mol dm^{-3}); (*b*) 21% O_2 (1.5×10^{-3} mol dm^{-3}); (*c*) 5.3% O_2 (3.8×10^{-4} mol dm^{-3}). All the continuous lines were calculated by using parameters derived as described in the text. The gradient of (*a*) varies from *ca.* 1 to *ca.* 0.5, and those of (*b*) and (*c*) are *ca.* 0.5. Initial concentrations are in mol dm^{-3} and initial rates in mol dm^{-3} s^{-1}

Mechanism (I)

$$[Ru_3L_3] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 3[RuL] \qquad (1)$$

$$[RuL] + O_2 \xrightarrow{k_2} \text{products} \qquad (2)$$

Mechanism (II)

$$[Ru_3L_3] \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Ru_2L_2] + [RuL] \qquad (3)$$

$$[RuL] + O_2 \xrightarrow{k_4} \text{products} \qquad (4)$$

$$[Ru_2L_2] + O_2 \xrightarrow{k_5} \text{products} \qquad (5)$$

Mechanism (IIIa)

$$[Ru_3L_3] \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Ru_2L_2] + [RuL] \qquad (3)$$

$$[RuL] + O_2 \xrightarrow{k_4} \text{products} \qquad (4)$$

$$[Ru_2L_2] \xrightarrow{k_6} ? \xrightarrow[\text{fast}]{O_2} \text{products} \qquad (6)$$

Mechanism (IIIb)

$$[Ru_3L_3] \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [Ru_2L_2] + [RuL] \qquad (3)$$

$$[RuL] \xrightarrow{k_7} ? \xrightarrow[\text{fast}]{O_2} \text{products} \qquad (7)$$

$$[Ru_2L_2] + O_2 \xrightarrow{k_5} \text{products} \qquad (5)$$

Mechanism (I)

$$R/c = k_1 - 27(k_{-1}/k_2^3)(R^3/c[O_2]^3) \qquad (8)$$

$$\text{or } R = 1/3(k_1/k_{-1})^{\frac{1}{3}}k_2[O_2]c^{\frac{1}{3}}[1 - (R/R_1)]^{\frac{1}{3}} \qquad (9a)$$

$$= 1/3(k_2/k_{-1}^{\frac{1}{3}})[O_2](R_1 - R)^{\frac{1}{3}} \qquad (9b)$$

Mechanism (II)

$$R/c = k_3 - (k_{-3}/k_4k_5)(R^2/c[O_2]^2) \qquad (10)$$

$$\text{or } R = (k_3k_4k_5/k_{-3})^{\frac{1}{2}}[O_2]c^{\frac{1}{2}}[1 - (R/R_3)]^{\frac{1}{2}} \qquad (11a)$$

$$= (k_4k_5/k_{-3})^{\frac{1}{2}}[O_2](R_3 - R)^{\frac{1}{2}} \qquad (11b)$$

Mechanism (IIIa)

$$R/c = k_3 - (k_{-3}/k_4k_6)(R^2/c[O_2]) \qquad (12)$$

$$\text{or } R \quad (k_3k_4k_6/k_{-3})^{\frac{1}{2}}[O_2]^{\frac{1}{2}}c^{\frac{1}{2}}[1 - (R/R_3)]^{\frac{1}{2}} \qquad (13a)$$

$$= (k_4k_6/k_{-3})^{\frac{1}{2}}[O_2]^{\frac{1}{2}}(R_3 - R)^{\frac{1}{2}} \qquad (13b)$$

Mechanism (IIIb)

$$R/c = k_3 - (k_{-3}/k_5k_7)(R^2/c[O_2]) \qquad (14)$$

$$\text{or } R = (k_3k_5k_7/k_{-3})^{\frac{1}{2}}[O_2]^{\frac{1}{2}}c^{\frac{1}{2}}[1 - (R/R_3)]^{\frac{1}{2}} \qquad (15a)$$

$$= (k_5k_7/k_{-3})^{\frac{1}{2}}[O_2]^{\frac{1}{2}}(R_3 - R)^{\frac{1}{2}} \qquad (15b)$$

The rate equations, in their non-integrated forms, for the three mechanisms are shown in equations (8)—(15) where $c = [Ru_3L_3]$, $R = -\mathrm{d}c/\mathrm{d}t$, $R_1 = k_1c$, and $R_3 = k_3c$. These equations are derived by making use of the steady-state approximation and the derivation of equation (12) is shown here as an example:

$$-\mathrm{d}[\mathrm{Ru_3L_3}]/\mathrm{d}t = k_3[\mathrm{Ru_3L_3}] - k_{-3}[\mathrm{Ru_2L_2}][\mathrm{RuL}] = R$$

$$\mathrm{d}[\mathrm{RuL}]/\mathrm{d}t = k_3[\mathrm{Ru_3L_3}] - k_{-3}[\mathrm{Ru_2L_2}][\mathrm{RuL}] - k_4[\mathrm{RuL}][\mathrm{O_2}] = 0$$

$$\mathrm{d}[\mathrm{Ru_2L_2}]/\mathrm{d}t = k_3[\mathrm{Ru_3L_3}] - k_{-3}[\mathrm{Ru_2L_2}][\mathrm{RuL}] - k_6[\mathrm{Ru_2L_2}] = 0$$

whence $[\mathrm{RuL}] = R/k_4[\mathrm{O_2}]$, $[\mathrm{Ru_2L_2}] = R/k_6$,

and $$R = R_3 - (k_{-3}/k_4k_6)(R^2/[\mathrm{O_2}])$$
$$\text{or } R/c = k_3 - (k_{-3}/k_4k_6)(R^2/c[\mathrm{O_2}]) \qquad (12)$$

Equation (10) is obtained from (12) by replacing k_6 by $k_5[\mathrm{O_2}]$, and equations (12) and (14) show why mechanisms (IIIa) and (IIIb) are kinetically indistinguishable, the form of the dependence of the rates on c and $[\mathrm{O_2}]$ being identical. A distinction between whether it is $[\mathrm{Ru_2L_2}]$ or $[\mathrm{RuL}]$ that is attacked by oxygen, would, therefore, have to be made on non-kinetic grounds.

Mechanism (I) can be distinguished from (II) and (III) by plotting R_0/c_0 against $R_0{}^3/c_0$ and $R_0{}^2/c_0$ at a constant value of $[\mathrm{O_2}]$. Figure 2 shows that a plot against $R_0{}^2/c_0$, for reactions under an atmosphere of pure oxygen, is an excellent straight line whereas that against $R_0{}^3/c_0$ shows pronounced curvature. Good linear plots of R_0/c_0 against $R_0{}^2/c_0$ were also obtained from the data at the other temperatures used and the intercepts on the ordinate axis can be taken as values of k_3. A linear least-squares analysis of the dependence of $\log(k_3/T)$ on $1/T$ leads to the parameters $\Delta H_3{}^\ddagger = 130.0 \pm 2.5$ kJ mol^{-1} (31.1 ± 0.6 kcal mol^{-1}) and $\Delta S_3{}^\ddagger = 64.2 \pm 7.5$ J K^{-1} mol^{-1} (15.3 ± 1.8 cal K^{-1} mol^{-1}). The percentage deviations ($\Delta k_3/\%$) of the four experimental values of k_3 from the ' least-squares ' values leads to a value of $[\Sigma(\Delta k_3/\%)^2/(4-2)]^{\frac{1}{2}}$ of 4.2% which is entirely consistent with the uncertainties in k_3 estimated by examination of the linear plots of R_0/c_0 against $R_0{}^2/c_0$. The uncertainties in the activation parameters can, therefore, be treated as reasonably good estimates of the standard deviations.

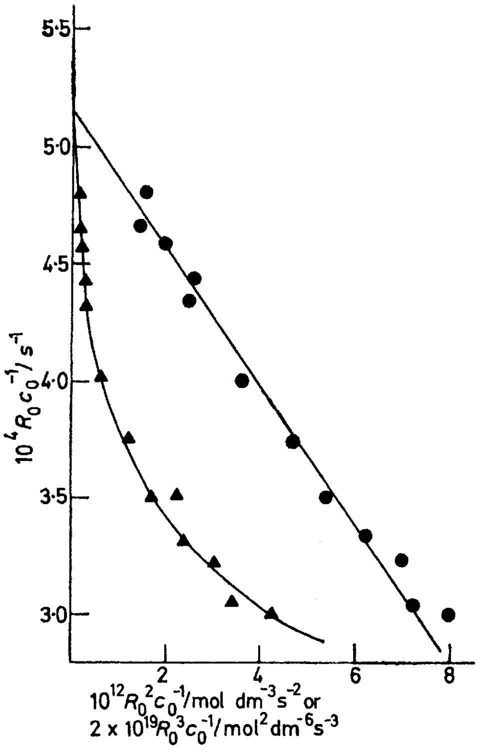

FIGURE 2 Dependence of $R_0c_0{}^{-1}$ on $R_0{}^2c_0{}^{-1}$ (●) and $R_0{}^3c_0{}^{-1}$ (▲) for reactions under 100% O_2 at 74.6 °C

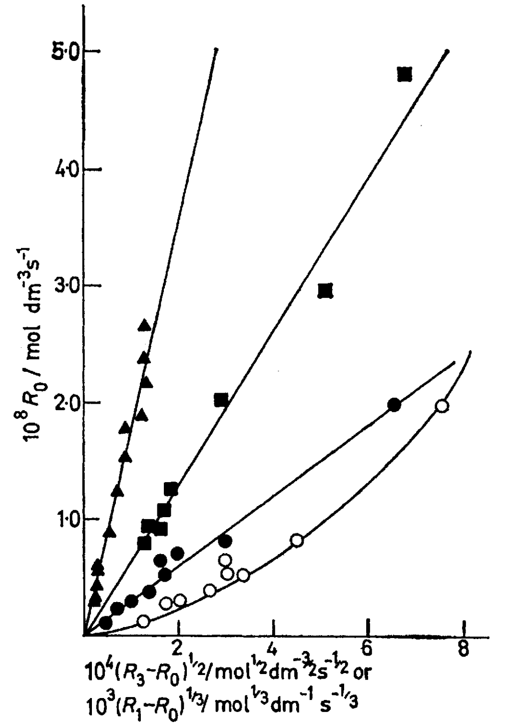

FIGURE 3 Dependence of initial rates at 74.6 °C on $(R_3 - R_0)^{\frac{1}{2}}$ $\{[\mathrm{O_2}] = 7.1 \times 10^{-3}$ (▲), 1.5×10^{-3} (■), or 3.8×10^{-4} mol dm^{-3} (●)$\}$ or $(R_1 - R_0)^{\frac{1}{3}}$ $\{[\mathrm{O_2}] = 3.8 \times 10^{-4}$ mol dm^{-3} (○)$\}$

Mechanism (I) can also be distinguished from (II) and (III) by plotting R_0 against $(R_1 - R_0)^{\frac{1}{3}}$ and $(R_3 - R_0)^{\frac{1}{2}}$ at a constant value of $[\mathrm{O_2}]$. The value of k_1 needed to calculate R_1 was estimated by extrapolation to $R_0{}^3/c_0 = 0$ of the curved plot (Figure 2) of R_0/c_0 against $R_0{}^3/c_0$ and is indistinguishable from k_3. Data obtained from reactions under an atmosphere of 5% oxygen (in an oxygen–nitrogen mixture) are plotted in these ways in Figure 3. Again the data plotted as for mechanisms (II) and (III) lead to an excellent straight line while those plotted according to (I) show obvious curvature. The two other linear plots in Figure 3 are those for mechanisms (II) and (III) from data for reactions under atmospheres of air or 100% oxygen.

A graphical distinction between mechanisms (II) and (III) can be made by plotting the gradients of the linear plots in Figure 3 against $[\mathrm{O_2}]$ or $[\mathrm{O_2}]^{\frac{1}{2}}$. For mechanism (II) the gradients should provide values for $(k_4k_5/k_{-3})^{\frac{1}{2}}[\mathrm{O_2}]$, and for mechanism (III) they should provide values for $(k_4k_6/k_{-3})^{\frac{1}{2}}[\mathrm{O_2}]^{\frac{1}{2}}$ or $(k_5k_7/k_{-3})^{\frac{1}{2}}[\mathrm{O_2}]^{\frac{1}{2}}$. Such plots are shown in Figure 4 and that against $[O_2]^{\frac{1}{2}}$ is clearly a good straight line while that against $[O_2]$ is a pronounced curve. The plots include data obtained under an atmosphere of 56.3% oxygen when only a very limited range of values of c_0 was used (Table 1) so that the ' gradient ' is simply the average value of $R_0/(R_3 - R_0)^{\frac{1}{2}}$.

This graphical analysis provides convincing evidence that the data are in excellent agreement with mechanism (III) rather than (I) or (II). A numerical analysis leads to exactly the same conclusion. Thus equations (9b), (11b), (13b), and (15b) enable one to calculate values of $k_2/k_{-1}^{\frac{1}{2}}$, $(k_4k_5/k_{-3})^{\frac{1}{2}}$, and $(k_4k_6/k_{-3})^{\frac{1}{2}}$ or $(k_5k_7/k_{-3})^{\frac{1}{2}}$ from each measurement of R_0 at a given value of $[O_2]$ if the values of k_1 and k_3 obtained graphically are used. Unweighted averages, and their unweighted standard deviations, are shown in Table 2. For runs under <100% oxygen the values of R were always well below R_1 or R_3 so that the absence of weighting has little effect. Almost half the values of R for runs under 100% oxygen were <0.5 (R_1 or R_3) and using only those data led to $10^3(k_4k_6/k_{-3})^{\frac{1}{2}} = 1.99 \pm 0.12\ s^{-\frac{1}{2}}$.

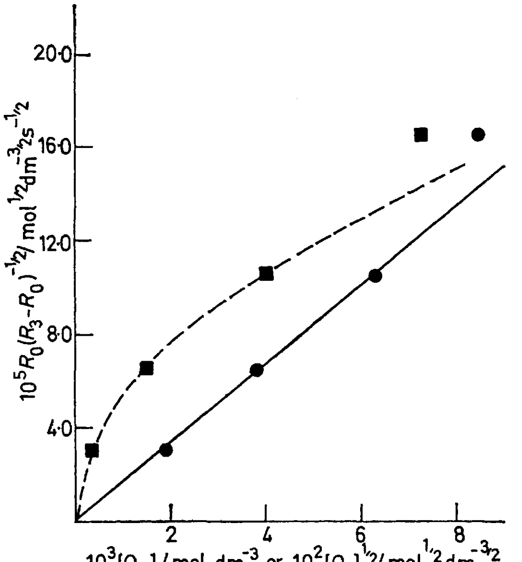

FIGURE 4 Dependence of $R_0(R_3 - R_0)^{-\frac{1}{2}}$ on $[O_2]^{\frac{1}{2}}$ (●) or $[O_2]$ (■) at 74.6 °C

Values of $k_2/k_{-1}^{\frac{1}{2}}$ were found to vary systematically with c_0 at constant $[O_2]$ and the average of these values is also dependent on $[O_2]$ so that mechanism (I) is not being followed. At a constant value of $[O_2]$, values calculated for $(k_4k_5/k_{-3})^{\frac{1}{2}}$ would not be expected to vary systematically with c_0 and they do not. They do vary substantially with $[O_2]$, however, thereby confirming that mechanism (II) is not being followed. In contrast the values calculated for $(k_4k_6/k_{-3})^{\frac{1}{2}}$ are essentially independent of $[O_2]$, the slightly higher value at $[O_2] = 7.1 \times 10^{-3}$ mol dm^{-3} being ascribable to a relatively small systematic error. Even this does not necessarily have to be invoked since it is possible that the rate of reaction (6) is governed by a two-term rate law of the form $k_6 = k_6' + k_6''[O_2]$ in which case k_4k_6/k_{-3} should be linearly dependent on $[O_2]$. The data are not sufficiently precise or extensive to verify this hypothesis, although it is evident that k_6'' must be relatively quite small. Finally, values of R_0 corresponding to all of the experimentally used sets of c_0 and $[O_2]$ at 74.6 °C were calculated by using $10^3(k_4k_6/k_{-3})^{\frac{1}{2}} = 1.6\ s^{-\frac{1}{2}}$ (for $10^3[O_2] =$ 0.38, 1.50, and 4.0 mol dm^{-3}) or 2.07 s$^{-\frac{1}{2}}$ (for $10^3[O_2] =$ 7.1 mol dm^{-3}), and $k_3 = 5.15 \times 10^{-4}\ s^{-1}$. Values of $[R_0(\text{calc.}) - R_0(\text{expt.})]/R_0(\text{calc.})$, listed in Table 1, were used to estimate a standard deviation of *ca.* 13% for an individual measurement of R_0. The continuous lines in Figure 1 are drawn through values of R_0 calculated as above. It may be concluded, therefore, that the data are in excellent accord with mechanism (III) and that (I) and (II) can definitely be excluded.

TABLE 2

Kinetic parameters calculated for mechanisms (I)—(III)

$10^3[O_2]$ / mol dm^{-3}	$10^3k_2/k_{-1}^{\frac{1}{2}}$ / dm mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$	$10^2(k_4k_5/k_{-3})^{\frac{1}{2}}$ / dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ s$^{-\frac{1}{2}}$	$10^3(k_4k_6/k_{-3})^{\frac{1}{2}}$ / s$^{-\frac{1}{2}}$
0.38	14.2 ± 1.9	8.13 ± 0.50	1.58 ± 0.10 (1.53) *
1.50	8.1 ± 0.7	4.10 ± 0.26	1.60 ± 0.10 (1.70) *
4.01	5.9 ± 0.6	2.5 ± 0.3	1.60 ± 0.18
7.11	5.5 ± 0.4	2.37 ± 0.15	2.07 ± 0.06 (2.11) *

* Values in parentheses are those estimated from the gradients of the linear plots in Figure 3.

The formulation of the two different fragments as $[\{Ru(CO)_3(PPh_3)\}_2]$ and $[Ru(CO)_3(PPh_3)]$ seems the most reasonable. The complex $[\{Fe(CO)_4\}_2]$ has been suggested[8] as an intermediate in reactions of $[Fe(CO)_4]$ and was formulated as $[(OC)_4Fe{=}Fe(CO)_4]$, complexes with Fe=Fe bonds now being quite well known.[9] The complex $[Ru(CO)_3(PPh_3)]$ is a four-co-ordinate d^8 species of a very well known type. However, it is not likely to be in a simple planar diamagnetic form for the following reasons. The complex $[Ru(CO)_4(PPh_3)]$ reacts with PPh_3 at 60 °C in hydrocarbon solvents by a CO-dissociative path[10] to form $[Ru(CO)_3(PPh_3)_2]$ and we find the yield to be quantitative even under an atmosphere of oxygen. The product is stable to oxygen for some hours under these conditions. The $[Ru(CO)_3(PPh_3)]$ intermediate formed in the CO-dissociative process is most likely to be the simple diamagnetic species and this is therefore much more reactive towards addition of PPh_3 than reaction with oxygen. In our reactions the proposed $[Ru(CO)_3(PPh_3)]$ intermediate would therefore be expected to form $[Ru(CO)_3(PPh_3)_2]$ in 33% yield if it were the same as that formed by CO dissociation from $[Ru(CO)_4(PPh_3)]$ and yet no product $[Ru(CO)_3(PPh_3)_2]$ was

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[8] I. Fischler, K. Hildenbrand, and E. Korner von Gustorf, *Angew. Chem., Internat. Edn.*, 1975, **14**, 54.

[9] E. Nicholas, L. S. Bray, R. E. Davis, and R. Pettit, *Chem. Comm.*, 1971, 608; H. J. Schmitt and M. L. Zeigler, *Z. Naturforsch.*, 1973, **B28**, 508; J. L. Calderon, S. Fontana, E. Frauendorfer, V. W. Day, and S. D. A. Iske, *J. Organometallic Chem.*, 1974, **64**, C16.

[10] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J.C.S. Dalton*, 1975, 1876.

detected. It seems not unreasonable to suppose, therefore, that the $[Ru(CO)_3(PPh_3)]$ formed by fragmentation of $[\{Ru(CO)_3(PPh_3)\}_3]$ is in the paramagnetic and, presumably, pseudo-tetrahedral form. {A similar isomerism to this has been proposed for $[Fe(CO)_4]$.[11]} Being a diradical, this might be expected to react readily with oxygen but, not having a completely empty acceptor orbital, it would not so readily add a further PPh_3 ligand. The increase in the rates to a limiting value with increasing $[PPh_3]$ suggests that the reaction of the intermediate with oxygen may be reversible, the adduct then reacting with PPh_3 to form PPh_3O, *i.e.* equation (4) should be replaced by (4a). Only when

$$[RuL] + O_2 \overset{k_4}{\rightleftharpoons} [RuL(O_2)] \xrightarrow{PPh_3} \text{products} \quad (4a)$$

$[PPh_3]$ is high enough does every adduct formed react with PPh_3 so that the rate of adduct formation becomes rate determining for that step. If the $[\{Ru(CO)_3(PPh_3)\}_2]$ fragment is formulated as diamagnetic $[(Ph_3P)(OC)_3Ru{=}Ru(CO)_3(PPh_3)]$ its relative unreactivity towards direct attack by oxygen can be more easily understood. These considerations suggest that mechanism (IIIa) rather than (IIIb) is operative.

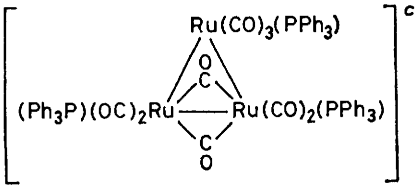
This formulation of the two fragments is convenient in that it is not inconsistent with our proposal[6] that $[\{Ru(CO)_3(PPh_3)\}_2]$ and $[Ru(CO)_3(PPh_3)]$ are also intermediates in the quantitative formation of $[Ru(CO)_3(PPh_3)_2]$ by reaction (16) in decalin at 120—150 °C. This reaction is independent of $[PPh_3]$ and [CO] and must

$$[\{Ru(CO)_3(PPh_3)\}_3] \xrightarrow{PPh_3\text{-}CO} 3[Ru(CO)_3(PPh_3)_2] \quad (16)$$

involve fragmentation at some stage. Direct formation of three $[Ru(CO)_3(PPh_3)]$ fragments seems unlikely since the reverse reaction (which is known to occur readily in closely related systems[12]) would have to be trimolecular. Rate-determining formation of $[\{Ru(CO)_3(PPh_3)\}_2]$ and $[Ru(CO)_3(PPh_3)]$ was, therefore, proposed.[6] In this case, however, the behaviour is consistent with the $[Ru(CO)_3(PPh_3)]$ being in the diamagnetic planar form. The kinetic parameters for this step[6] [$\Delta H^{\ddagger}$ 148 kJ mol^{-1}, $\Delta S^{\ddagger}$ 30 J K^{-1} mol^{-1}, and k (100 °C) 5.7×10^{-7} s^{-1}] are much less favourable than those reported here for reaction (3). There is no obvious explanation for these relative rates but they may represent another example of the more rapid formation of thermodynamically less-stable species. The fact that reaction (3) is reversible accounts for the fact that, according to the first-order rate constants for the two fragmentation processes, for each occasion that (16) occurs at 100 °C, (3) has occurred over 10^4 times. Indeed, under the conditions where $[\{Ru(CO)_3(PPh_3)\}_3]$ is proposed to fragment into $[\{Ru(CO)_3(PPh_3)\}_2]$ and diamagnetic $[Ru(CO)_3(PPh_3)]$ several reactions must be occurring at relatively very rapid rates, but reversibly so that no products are seen. This is illustrated in Table 3 which shows that at 100 °C and in the presence of appreciable amounts of free CO and PPh_3 the $[\{Ru(CO)_3(PPh_3)\}_3]$ complex is a very dynamic species indeed and this must be so even if the mechanistic details of each process are not exactly as proposed.

TABLE 3

Kinetic data for reactions of $[\{Ru(CO)_3(PPh_3)\}_3]$ in decalin

Reaction	Temperature range[a] (θ_c/°C)	k (100 °C) / s^{-1}	$\Delta H^{\ddagger}$ / kJ mol^{-1}	$\Delta S^{\ddagger}$ / J K^{-1} mol^{-1}	Ref.
$\longrightarrow [\{Ru(CO)_3(PPh_3)\}_2]$ + diamagnetic $[Ru(CO)_3(PPh_3)]$	140—170	6×10^{-7}	148	30	6
$\rightleftharpoons [Ru_3(CO)_8(PPh_3)_3]$[b] + CO	120—160	1×10^{-5}	138	27	6
$\rightleftharpoons [\{Ru(CO)_3(PPh_3)\}_2]$ + paramagnetic $[Ru(CO)_3(PPh_3)]$	55—75	1×10^{-2}	130	64	This work
$\rightleftharpoons [Ru_3(CO)_9(PPh_3)_2]$[b] + PPh_3	40—70	2×10^{-1}	123	69	6
$\rightleftharpoons$  [c]	−100	Very fast			d

[a] For convenient study. [b] Probably in reactive form with one broken Ru–Ru bond.[6] [c] By analogy with the known very rapid CO-migration reaction of $[\{Ru(CO)_4\}_3]$. [d] A. Forster, B. F. G. Johnson, J. Lewis, T. W. Matheson, B. H. Robinson, and W. G. Jackson, *J.C.S. Chem. Comm.*, 1974, 1042; S. Aime, O. Gambino, L. Milone, E. Sappa, and E. Rosenberg, *Inorg. Chim. Acta*, 1975, **15**, 53.

The fact that free PPh_3 is needed for the reaction to proceed smoothly also implies that the intermediate formed by PPh_3 dissociation does not react cleanly with oxygen. By contrast the intermediates $[\{Ru(CO)_3(PPh_3)\}_2]$ and paramagnetic $[Ru(CO)_3(PPh_3)]$ react smoothly in the presence of oxygen to form the yellow product and 1 mol of PPh_3O per mol of Ru. The yellow product is not the simple adduct $[Ru(CO)_2(O_2)(PPh_3)_2]$[13] and further work is necessary to elucidate its structure and that of the green species that catalytically oxidizes PPh_3.

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