Mechanism of the Conversion of $[Ru(CO)_5]$ into $[Ru_3(CO)_{12}]$ †

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The conversion of $[Ru(CO)_5]$ into $[Ru_3(CO)_{12}]$ in cyclohexane at 294—308 K has been shown to involve initial carbon monoxide dissociation to give the intermediate $[Ru(CO)_4]$; the latter then combines further with $[Ru(CO)_5]$ in a series of fast steps to form ultimately the trimer $[Ru_3(CO)_{12}]$. The mechanism is thus closely related to the dissociative mechanism demonstrated previously for substitution of one CO of $[Ru(CO)_5]$ by PPh_3, and essentially identical activation parameters are found for both types of reactions [for the 'trimerization', $\Delta H^{\ddagger} = 109\ (\pm 15)$ kJ mol^{-1}, $\Delta S^{\ddagger}$ 53 ($\pm$15) J K^{-1} mol^{-1}]. The equilibrium constant for the reaction $3[Ru(CO)_5] \rightleftharpoons [Ru_3(CO)_{12}] + 3CO$ at 298 K is 3.0 ($\pm$0.5) × 10^{6} mol dm^{-3}.

We have recently demonstrated the utilization of monomeric $[Ru(CO)_5]$ to develop Fischer–Tropsch catalyst precursors containing the relatively bulky, trimeric $[Ru_3(CO)_{12}]$ encapsulated in the supercages of NaY zeolite.[1] During the course of this work we also reported the synthesis and characterization of a new binary ruthenium carbonyl, the oligomeric $[\{Ru(CO)_4\}_n]$.[2]

Prior to this investigation, only three binary carbonyl compounds of ruthenium had been known, $[Ru(CO)_5]$, $[Ru_2(CO)_9]$, and $[Ru_3(CO)_{12}]$.[3] Of these, $[Ru_3(CO)_{12}]$ is thermodynamically the most stable, and is formed spontaneously when either of the others is allowed to stand in the absence of a partial pressure of CO [equations (1) and (2)]. The

$$3[Ru(CO)_5] \rightleftharpoons [Ru_3(CO)_{12}] + 3CO \qquad (1)$$

$$2[Ru_2(CO)_9] \longrightarrow [Ru_3(CO)_{12}] + [Ru(CO)_5] + CO \qquad (2)$$

monomeric $[Ru(CO)_5]$ can be prepared quantitatively in solution from $[Ru_3(CO)_{12}]$ under CO pressure either thermally[4] or photochemically,[5a] and thus equation (1) is reversible under a partial pressure of CO. However, while the mechanism of the photochemical fragmentation process has received considerable attention,[5] neither the mechanism of the formation of $[Ru_3(CO)_{12}]$ from the monomer nor the equilibrium constant for equation (1) have been determined.

Inasmuch as syntheses of the new catalysts involved diffusion of $[Ru(CO)_5]$ under CO pressure into the pores of the zeolite, followed by removal of the CO pressure and irreversible conversion of the monomer into $[Ru_3(CO)_{12}]$ [equation (1)],[1] it seemed desirable to gain some understanding of the nature of the latter process. Little is known in fact concerning the mechanisms of the formation of metal carbonyl clusters in general, and we now present both an account of a mechanistic study of the thermal conversion of $[Ru(CO)_5]$ into $[Ru_3(CO)_{12}]$ and an estimate of the equilibrium constant for this process.

Experimental

Infrared spectra were run in the absorbance mode on a Bruker IFS-85 FTIR spectrometer, while photochemical reactions were performed utilizing a Hanovia lamp positioned about 1 cm from reaction mixtures enclosed in a water-cooled, quartz apparatus. All manipulations of compounds were carried out under an atmosphere of CO or N_2.

The compound $[Ru_3(CO)_{12}]$ was synthesized from $RuCl_3 \cdot 3H_2O$ and CO (50 atm) in methanol as in the literature,[6] while solutions of $[Ru(CO)_5]$ for kinetic purposes were synthesized by photolyzing solutions of $[Ru_3(CO)_{12}]$ ($\approx$0.10 mmol) in dry, degassed cyclohexane (200 cm^3) under 1 atm of CO for 10 min. The thus formed colourless solutions of $[Ru(CO)_5]$ [ν(CO) 2 037s and 2 001vs cm^{-1}][3,4] were indefinitely stable under 1 atm of CO, but were found to revert over 2 h with bubbling N_2 to the orange $[Ru_3(CO)_{12}]$ [ν(CO) 2 061vs, 2 032s, and 2 012m cm^{-1}].[3,4]

Solutions of monomer prepared in this way ($\approx$ 1.5 × 10^{-3} mol dm^{-3}) were subjected to successive freeze–thaw cycles in order to remove CO, covered with aluminium foil to exclude light, and placed in a constant-temperature water-bath regulated to ±0.5 °C with a Haake E3 apparatus. For kinetic studies, N_2 was bubbled through the stirred solutions (20 cm^3 min^{-1}), and the course of the conversion of $[Ru(CO)_5]$ into $[Ru_3(CO)_{12}]$ over the temperature range 294—308 K was monitored utilizing the ν(CO) of $[Ru_3(CO)_{12}]$ at 2 061 cm^{-1} [ε 3.76 ($\pm$0.06) × 10^4 dm^3 mol^{-1} cm^{-1}] or the ν(CO) of $[Ru(CO)_5]$ at 2 001 cm^{-1} [ε 1.38 ($\pm$0.1) × 10^4 dm^3 mol^{-1} cm^{-1}]. Under identical experimental conditions, solutions of $[Ru(CO)_5]$ were treated, with constant nitrogen bubbling, at 303 K with a 75-fold molar excess of PPh_3, the ν(CO) at 2 001 cm^{-1} being monitored. Infrared spectra taken during the course of the kinetic run showed that the predominant product was $[Ru(CO)_4(PPh_3)]$ [ν(CO) 2 061s, 1 987m, and 1 954vs cm^{-1}],[5a] negligible amounts of the disubstituted product $[Ru(CO)_3(PPh_3)_2]$ [ν(CO) 1 897 cm^{-1}] being formed.

In a variation of the above, a 100-cm^3 sample approximately 3.0 × 10^{-3} mol dm^{-3} in $[Ru(CO)_5]$ in cyclohexane was purged with a CO–N_2 gas mixture containing 5.32% CO (Liquid Carbonic). The solution was maintained at 303 K under a large volume of the gas mixture in the dark for 48 h ($\approx$ 2.5 half-lives), during which time the variation in $[Ru(CO)_5]$ was monitored.

All runs were repeated two or three times, with degrees of reproducibility as indicated in the rate constant data given below.

To determine the equilibrium constant for equation (1), a solution of 0.0199 g $[Ru_3(CO)_{12}]$ in heptane (100 cm^3) was degassed, placed in a Parr Stirring Minireactor, and stirred

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† *Supplementary data available* (No. SUP 56767, 5 pp.): derivation of the rate equation. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. unit employed: atm = 101 325 Pa.

continuously under a CO pressure of 39 ± 1 atm at 298 K for 6 months. During this period, samples were withdrawn non-invasively *via* a sampling tube approximately once a month and analyzed rapidly by i.r. spectroscopy.

Results and Discussion

Kinetic Studies.—The conversion of $[Ru(CO)_5]$ into $[Ru_3(CO)_{12}]$ is retarded considerably by the presence of CO in solution, and thorough degassing of the solutions was necessary before all kinetics runs. Thus preliminary kinetic experiments for the conversion under a static pressure of N_2 rather than with nitrogen bubbling exhibited first-order behaviour in monomer for only about 20 min. Progressive slowing of the reaction resulted because of build-up of the carbon monoxide concentration and the consequently increasing significance of the reverse process.

It was therefore decided to employ nitrogen bubbling in order to remove CO as it formed and to prevent the back reaction. Slight increases in the total ruthenium concentrations were noted during some runs because of solvent evaporation, but the errors introduced by this factor were found to be negligible except for the runs at 308 K. The latter were accordingly carried out for shorter periods of time under static nitrogen pressure as outlined above.

Under these conditions, reactions reproducibly exhibited first-order kinetics for the loss of $[Ru(CO)_5]$ over >3 half-lives, with observed first-order rate constants ($k_{obs.}$) of 1.1 (±0.1) × 10^{-4}, 1.7 (±0.2) × 10^{-4}, 4.2 (±0.5) × 10^{-4}, and 6.0 (±0.6) × 10^{-4} s^{-1} at 294, 298, 303, and 308 K, respectively.

Given the slowing of the reaction when the CO produced was not swept away, we postulate that the rate-determining step of equation (1) involves the reversible dissociation of one CO [equation (3)]. Reasonable subsequent fast steps are (4) and (5).

$$[Ru(CO)_5] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(CO)_4] + CO \qquad (3)$$

$$[Ru(CO)_4] + [Ru(CO)_5] \xrightarrow[\text{fast}]{k_2} [Ru_2(CO)_9] \qquad (4)$$

$$[Ru_2(CO)_9] + [Ru(CO)_5] \xrightarrow[\text{fast}]{k_3} [Ru_3(CO)_{12}] + 2CO \qquad (5)$$

Assuming the steady-state approximation for the concentrations of $[Ru(CO)_4]$ and $[Ru_2(CO)_9]$, and taking into account the fact that [CO] is negligible, the loss of $[Ru(CO)_5]$ should obey expression (6).

$$-d[Ru(CO)_5]/dt = 3k_1[Ru(CO)_5] \qquad (6)$$

On the basis of this analysis, one would therefore expect the rate of disappearance of $[Ru(CO)_5]$ in the absence of CO to be first order in the concentration of $[Ru(CO)_5]$, as is observed, and $k_{obs.}$ to be equal to $3k_1$. Values of k_1 at 294, 298, 303, and 308 K are therefore 0.37 (±0.03) × 10^{-4}, 0.57 (±0.06) × 10^{-4}, 1.4 (±0.2) × 10^{-4}, and 2.0 (±0.2) × 10^{-4} s^{-1}, respectively. Activation parameters were found to be E_a 111 (±15) kJ mol^{-1}, $\Delta H^\ddagger$ 109 (±15) kJ mol^{-1}, and $\Delta S^\ddagger$ 53 (±15) J K^{-1} mol^{-1}.

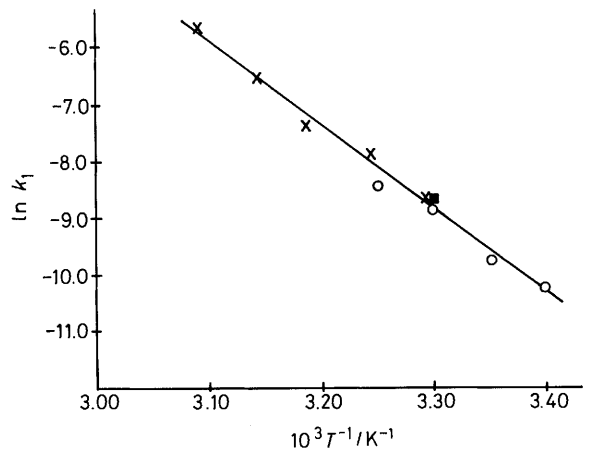

Figure 1. Arrhenius plot utilizing k_1 values for the conversion of $[Ru_3(CO)_{12}]$ into $[Ru(CO)_5]$ under bubbling N_2 (○), for the CO substitution of $[Ru(CO)_5]$ with PPh_3 (■), and from ref. 5*a* (X)

The first step in this mechanism, represented by equation (3), is identical to the initial, slow step proposed by Poë and co-workers[5a] for the substitution of one CO of $[Ru(CO)_5]$ by PPh_3 under a partial pressure of CO (discussed below). The mechanism for the substitution process studied here, in which the back reaction associated with k_{-1} is negligible, is as in equations (3) and (7). Thus, since both the CO substitution

$$[Ru(CO)_5] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ru(CO)_4] + CO \qquad (3)$$

$$[Ru(CO)_4] + PPh_3 \xrightarrow[\text{fast}]{k_4} [Ru(CO)_4(PPh_3)] \qquad (7)$$

$$-d[Ru(CO)_5]/dt = k_1[Ru(CO)_5] \qquad (8)$$

$$k_1 = k_{obs.} \qquad (9)$$

reaction studied here and by Poë and the conversion of $[Ru(CO)_5]$ into $[Ru_3(CO)_{12}]$ studied here are believed to share a common, rate-determining initial step [equation (3)], the k_1 values obtained in the two studies should be identical. However, as mentioned above, the Poë study was carried out under a partial pressure of CO, and, in order to test the comparison of the mechanism and values of k_1, the kinetics of the substitution reaction of $[Ru(CO)_5]$ with a large excess of PPh_3 were carried out with nitrogen bubbling through the solution such that the k_{-1} step was not a factor.

To our great pleasure, the substitution reaction of $[Ru(CO)_5]$ with PPh_3 exhibited first-order behaviour in $[Ru(CO)_5]$ over >3 half-lives in two separate experiments, the first-order rate constant k_1 at 303 K being 1.68 (±0.05) × 10^{-4} s^{-1}. This is identical, within experimental error, to the value of k_1 at 303 K found above for the formation of $[Ru_3(CO)_{12}]$. In addition, while Poë and co-workers[5a] do not quote values for k_1 (k_{-CO} in their study), a calculation utilizing the rate equation and data they present as well as data from the literature for [CO] values[7] leads to a value of k_1 at 303.4 K of 1.83 (±0.09) × 10^{-4} s^{-1} for CO substitution in the presence of CO, very similar to the values reported here for the two types of reactions of $[Ru(CO)_5]$. In addition, we note the similarity in activation parameters above and those of Poë and co-workers [E_a 117.5 (±2) kJ mol^{-1}, $\Delta H^\ddagger$ 115 (±2) kJ mol^{-1}, and $\Delta S^\ddagger$ 63.5 (±5.4) J K^{-1} mol^{-1}], and call attention to the linearity of the Arrhenius plot obtained by utilizing the three sets of k_1 values (Figure 1).

Having confirmed that the kinetic data obtained in the absence of CO obeyed the rate law based on the mechanism proposed for the conversion of $[Ru(CO)_5]$ into $[Ru_3(CO)_{12}]$, experiments were undertaken in the presence of a small, essentially constant concentration of CO. We wished to test further the conformity with the proposed mechanism and, if possible, to determine the relative values of k_1, k_{-1}, and k_2. The rate of conversion of $[Ru(CO)_5]$ into $[Ru_3(CO)_{12}]$ at 303 K under a large, steady head of 5.32% CO in N_2 was therefore investigated, as above for experiments under pure N_2.

Assuming the applicability of Henry's law to the literature data for [CO] values, the concentration of CO in the reaction solution under the CO–N_2 mixture was 4.9 × 10^{-4} mol dm^{-3} (as compared to a saturation concentration at 303 K of 9.2 × 10^{-3} mol dm^{-3}).[7] This is only about 1/6 of the initial concentration of

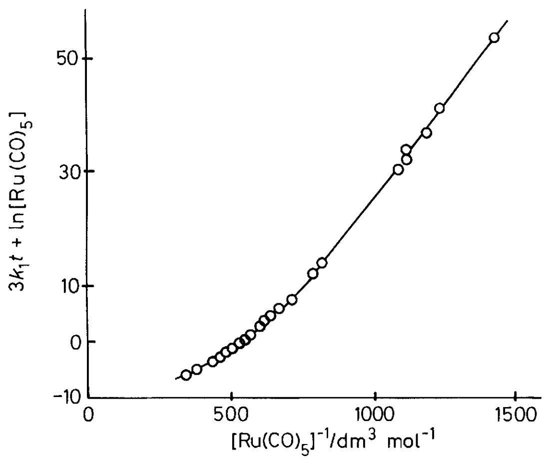

Figure 2. Plot of $3k_1t + \ln[Ru(CO)_5]$ *vs.*$[Ru(CO)_5]^{-1}$ for the conversion of $[Ru_3(CO)_{12}]$ into $[Ru(CO)_5]$ under a low partial pressure of CO

$[Ru(CO)_5]$, and it was hoped that the rate of exchange of N_2 and CO across the liquid–vapour boundary would be sufficient to ensure that a constant concentration of dissolved CO would pertain at a level low enough for the reaction to proceed at a measurable rate. When this (unknown) steady state was reached, the rate of disappearance of $[Ru(CO)_5]$ would obey the more complex rate law, derived (see SUP 56767) assuming steady-state concentrations of $[Ru(CO)_4]$ and $[Ru_2(CO)_9]$, shown in equation (10). Thus a plot of $3k_1t + \ln[Ru(CO)_5]$

$$\frac{k_{-1}[CO]}{k_2[Ru(CO)_5]} = 3k_1t + \ln[Ru(CO)_5] \qquad (10)$$

vs. $[Ru(CO)_5]^{-1}$ should give a straight line with a slope $[CO]k_{-1}/k_2$, and the ratio k_{-1}/k_2 can be obtained if [CO] can be estimated. Figure 2 shows such a plot, entirely reproducible and obtained using an average of the k_1 values determined in the kinetic experiments described above.

The first portion of the plot represents the brief time period, early in the reaction, during which the total CO concentration in solution was perhaps too low to inhibit the reaction significantly. As would be anticipated, first-order kinetics are observed. As the reaction proceeded, however, [CO] increased and the reacting system entered the regime where exchange with the CO—N_2 atmosphere was sufficient to maintain an essentially constant CO concentration in solution. The straight-line portion of the plot {up to the point where 85% of the $[Ru(CO)_5]$ had been consumed} thus confirms the validity of the rate law (10).

Although [CO] was not known, it must have lain between 4.9×10^{-4} (arising from the atmosphere, see above) and 2.7×10^{-3} mol dm^{-3} {arising from the atmosphere and assuming all of the $[Ru(CO)_5]$ contributed to the free CO}. Thus $24 \leqslant k_{-1}/k_2 \leqslant 132$. The observation that $k_{-1} \gg k_2$ is not surprising, as reaction of the unsaturated, sixteen-electron species $[Ru(CO)_4]$ might well be more facile with CO than with the much larger $[Ru(CO)_5]$. Furthermore, although the treatment provided here does not permit estimation of the rate constants, the general features of the plot shown in Figure 2 do seem to confirm that the relationship derived from the mechanism proposed is correct, and that the mechanism proposed is indeed operative.

After this manuscript had been submitted, there appeared a paper in which transient i.r. spectroscopy was used to study co-ordinatively unsaturated ruthenium carbonyls formed by excimer laser photolysis of $[Ru(CO)_5]$;[8] gas-phase rate constants corresponding to our k_{-1} and k_2 were found to be $\approx 5 \times 10^9$ and $\approx 10^{10}$ dm^3 mol^{-1} s^{-1}, respectively. Although these gas-phase data cannot be related to the rate constants found in solution, we note that both are near or in excess of the upper limit for a second-order rate constant as calculated by the authors.[8] While the results are consistent with our assumptions concerning the high reactivity of $[Ru(CO)_4]$, it is not clear, given the uncertainties in the gas-phase rate measurements, that the finding that $k_2 \gg k_{-1}$ in the gas phase, contrary to our findings in solution, is significant.

Equilibrium Constant Determination.—As described in the Experimental section, a solution of $[Ru_3(CO)_{12}]$ in n-heptane under a pressure of 39 atm was allowed to come to equilibrium over 6 months. The concentrations of $[Ru(CO)_5]$ and $[Ru_3(CO)_{12}]$ were determined non-invasively at various time intervals using the ν(CO) at 2 001 and 2 061 cm^{-1}, and it was found that the ratio $[Ru_3(CO)_{12}]/[Ru(CO)_5]$ levelled off at 1.1 ± 0.2. Assuming that the solubility of CO (0.0118 mol dm^{-3}, ref. 9) in n-heptane at 298 K and 1 atm can be extrapolated linearly to the much higher pressure utilized here, [CO] is determined to be 0.46 mol dm^{-3} and the equilibrium constant for equation (1) is $3.0\ (\pm 0.5) \times 10^6$ mol dm^{-3}. Thus, under 1 atm CO, the concentration of $[Ru(CO)_5]$ will be about four orders of magnitude less than that of $[Ru_3(CO)_{12}]$, explaining the oft made observations that the former decomposes completely to the latter.

Acknowledgements

Financial assistance from the U.S. Office of Naval Research made this research possible. We are also indebted to the International Nickel Company of Canada and Johnson-Matthey for loans of ruthenium trichloride, and to A. J. Poë, J. A. Stone, and D. H. Macartney for helpful discussions.

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Received 17*th February* 1989; *Paper* 9/00750D