Reaction Mechanisms of Metal–Metal Bonded Carbonyls: $Re_2(CO)_{10}$

By L. I. B. HAINES and A. J. POË*

(*Department of Chemistry, Imperial College of Science and Technology, London, S.W.7*)

KINETIC studies of reactions of the metal–metal bonded carbonyls, $Mn_2(CO)_{10}$[1] and $Co_2(CO)_6(PBu^n{}_3)_2$,[2] have been interpreted as providing at least a lower limit for the activation enthalpy required to produce homolytic fission of the metal–metal bonds. We now report analogous studies of reactions of $Re_2(CO)_{10}$ (in decalin between 130 and 150°) which support the mechanism assigned to the reactions of these complexes.

The pseudo-first-order rate constants for substitution with PPh_3 to form $Re_2(CO)_9(PPh_3)$ and $Re_2(CO)_8(PPh_3)_2$ rise to a limiting value with increasing $[PPh_3]$, and the limiting rate is unaffected by the presence of 1 atmos. of carbon monoxide. The rate constants for decomposition to form products containing no co-ordinated carbon monoxide rise with increasing $[O_2]$, and the rate under 1 atmos. of O_2 is identical with the limiting rate of substitution with PPh_3. The Arrhenius plots for the limiting rates of substitution and for decomposition in solutions equilibrated with oxygen are both linear ($\Delta H^\ddagger = 38{\cdot}6 \pm 0{\cdot}4$ kcal./mole, $\Delta S^\ddagger = 13{\cdot}7 \pm 1{\cdot}0$ cal.mole^{-1} deg.$^{-1}$) whereas those for the decompositions in solutions equilibrated with air or in the absence of oxygen are curved, the rates being relatively lower the higher the temperature. The reaction with iodine follows the pseudo-first-order rate law: $k_{obs} = k_a + k_b[I_2]$ ($\Delta H_b{}^\ddagger = 17{\cdot}4$ kcal./mole, $\Delta S_b{}^\ddagger = -24$ cal.mole^{-1}deg.$^{-1}$). The values of k_b/k_a are so large that k_a is not accurately obtainable but the values are equal to the rates of decomposition under oxygen within the experimental uncertainty.

The major differences from the reactions of $Mn_2(CO)_{10}$ are the absence of any retardation of the limiting rates of substitution by 1 atmos. of carbon monoxide, and the identity of the limiting rates of substitution and of decomposition under oxygen. Minor differences are the lack of dependence on [PPh_3] of the ratios of initial rates of formation of the mono- and bis-phosphine complexes, and the formation of substantial amounts of the di-iodo-octacarbonyl dimer in addition to the iodopentacarbonyl monomer on reaction with iodine.

These results can all be explained in terms of the basic scheme shown. The excited intermediate can be formulated as a carbonyl-bridged species,

$$\begin{tikzcd}
Re_2(CO)_{10} \arrow[r, shift left, "k_1"] & \text{Excited intermediate} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2"'] \arrow[dr, "\text{Reactant}", "k_3"'] & \\
& \text{Decomposition} & \text{Oxidation or substitution products}
\end{tikzcd}$$

$(CO)_4Re(CO)Re(CO)_5$, with no metal–metal bond and with one Re atom co-ordinatively unsaturated. The activation enthalpy, $\Delta H_1^{\ddagger} = 38{\cdot}6$ kcal./mole, is a lower limit for that needed to produce homolytic fission of the Re–Re bond. The lack of retardation by CO of the limiting rates of substitution suggests that no reaction which involves rate-determining dissociation of CO is occuring. This can be understood by considering the small difference in $\Delta H^{\ddagger}$ ($0{\cdot}3 \pm 1{\cdot}7$ kcal./mole) for the dissociative reactions of $Cr(CO)_6$ and $W(CO)_6$,[3] the relative slowness of the reaction of the latter being due to a value of $\Delta S^{\ddagger}$ more unfavourable by $8{\cdot}8 \pm 4{\cdot}0$ cal.mole^{-1}deg.$^{-1}$. If the dissociative reaction of $Re_2(CO)_{10}$ is governed by the same activation enthalpy as that of $Mn_2(CO)_{10}$, but by an activation entropy about 10 cal.mole^{-1}deg.$^{-1}$ less favourable, then the dissociative reaction of $Re_2(CO)_{10}$ would not be detected above 130°.

The ratio of the values of $\Delta H_1^{\ddagger}$ for the manganese and rhenium carbonyls ($1:1{\cdot}0_7$) is quite close to the ratio of the force constants for the metal–metal bonds ($1:1{\cdot}1_4$) obtained from studies of their Raman spectra.[4] The temperature dependence of the ratio k_{-1}/k_2 gives a value of 19 ± 3 kcal./mole for $\Delta H_{-1}^{\ddagger} - \Delta H_2^{\ddagger}$. This value is consistent with the results for the decomposition in the gaseous phase between 250 and 420°.[5] Under these conditions $\Delta H_{\text{obs}}^{\ddagger} = \Delta H_1^{\ddagger} - \Delta H_{-1}^{\ddagger} + \Delta H_2^{\ddagger}$ and our estimate of $\Delta H_{\text{obs}}^{\ddagger}$ is $19{\cdot}6 \pm 3$ kcal./mole as compared with the measured value of 17·4 kcal./mole.[5] In spite of the differences in the phases in which the reactions were occurring, the rates of decomposition at the higher temperatures, calculated by extrapolation of our results, are in excellent agreement with Ginzberg's values. The consistency between our results and those obtained for the gas-phase reaction tends to support our formulation of the reactive intermediate as a carbonyl-bridged dimer rather than the original formulation of it as a radical pair trapped in a solvent cage.[6]

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