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RECENT KINETIC STUDIES OF METAL–METAL BONDED CARBONYLS

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A INTRODUCTION

A very wide variety of polynuclear metal carbonyls containing metal–metal bonds has been prepared, and the structures and reactions of these complexes have been well characterised[1] However, relatively few thorough kinetic studies have been made in order to investigate whether there are any mechanistic features uniquely attributable to the presence of metal–metal bonds[2]. Quantitative studies related to the strengths of the metal–metal bonds are also still rather rare, and the relationship between the results given by the various techniques is not well understood[3]

An early kinetic study of the reaction of alkynes with dicobalt octacarbonyl indicated that reversible formation of a reactive carbonyl intermediate occurred[4], and kinetic evidence has also been obtained for similar formation of reactive intermediates in a variety of reactions involving $Mn_2(CO)_{10}$ (ref 3), $Re_2(CO)_{10}$ (ref 5), $[Co(CO)_3PBu_3]_2$ (ref 6) and $[CpFe(CO)_2]_2$ (ref 7). It has been suggested[3] that these intermediates can be formulated as species containing a single carbonyl bridge formed by a process of "metal migration"[3,8] roughly analogous to the well-characterised process of methyl migration[9] These intermediates have one metal atom with a vacant coordination site at which further attack by a variety of reagents can occur A general reaction scheme for a variety of reactions of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ has been suggested[5] The process of metal migration can be envisaged as involving concerted heterolytic fission of the metal–metal bond and nucleophilic attack, by the reduced metal atom, on the carbon atom of a carbon monoxide molecule coordinated to the oxidised metal atom. The degree to which the kinetic parameters for formation of this type of intermediate reflect the strengths of the metal–metal bonds will depend on the relative contributions of bond-making and bond-breaking to the process Raman[10], mass spectrometric[11], electrochemical[12] and theoretical[13] studies all indicate that the metal–metal bond in $Re_2(CO)_{10}$ is stronger than that in $Mn_2(CO)_{10}$, and the free energies and enthalpies of activation for formation of the reactive intermediate are also greater[5] for $Re_2(CO)_{10}$

We have continued to study the kinetics of reactions of related metal–metal bonded carbonyls in an attempt to verify the nature of the reactive intermediates involved, and to see to what extent relative values of the metal–metal bond strengths might be inferable from the kinetic parameters. Reactions in inert aliphatic hydrocarbon solvents have been studied by making use of UV–visible and infrared spectroscopy. Unless otherwise specified, first-order loss of reactant carbonyl was observed.

B. RESULTS

(i) Reactions of $MnRe(CO)_{10}$

The kinetics of the substitution reaction of this complex with triphenylphosphine, of the reaction with oxygen, and of the thermal decomposition reaction (all in decalin, and over a temperature range from 110 to 155°C) follow a similar kinetic pattern to those observed for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for formation of the reactive intermediate are 38.9 ± 0.2 kcal/mole and +18.5 ± 0.5 cal mole^{-1} deg^{-1}, respectively (uncertainties are standard deviations).

(ii) The reaction $Re_2(CO)_9PPh_3 + PPh_3 \rightleftharpoons [Re(CO)_4PPh_3]_2 + CO$

This reaction can be made to go to completion in either direction or to approach an equilibrium mixture, depending on the conditions employed. The reaction of $[Re(CO)_4PPh_3]_2$ with carbon monoxide is retarded by the presence of free triphenylphosphine, even when the reaction goes to completion. This retardation indicates the presence of a reactive intermediate, but not necessarily one formed by reversible dissociation of a triphenylphosphine ligand, similar behaviour being expected also for the metal migration mechanism[5]. For the present, and for the sake of discussion, we choose to assign the slow step to the metal migration process. Kinetic parameters for the forward reaction are $\Delta H^{\ddagger} = 34.8 \pm 0.3$ kcal/mole and $\Delta S^{\ddagger} = 7.7 \pm 0.7$ cal.mole^{-1} deg^{-1}, while for the reverse reaction $\Delta H^{\ddagger} = 38.8 \pm 0.5$ kcal/mole and $\Delta S^{\ddagger} = 21.5 \pm 1.5$ cal mole^{-1} deg^{-1}.

(iii) Reactions of $[Mn(CO)_4PPh_3]_2$

Reaction with triphenylphosphine in the absence of oxygen proceeds quite slowly, infrared bands at 1988w, 1938m and 1861s cm^{-1} being observed to grow. The reaction rate is half order with respect to $[Mn(CO)_4PPh_3]_2$ and zero order with respect to triphenylphosphine. These observations are consistent with slow reversible homolytic fission of the Mn–Mn bond as the initial step, the next step being the dissociative replacement of one carbon monoxide ligand in $Mn(CO)_4PPh_3$ to form $Mn(CO)_3(PPh_3)_2$.

Reaction of the complex with oxygen at 1 atm proceeds about 100 times faster than the reaction with triphenylphosphine and is first order with respect to $[Mn(CO)_4PPh_3]_2$

Complete loss of all CO stretching bands occurs, the unidentified products being assumed to be oxides of manganese The reaction is not retarded by added triphenylphosphine at concentrations up to 0 2 M At the lower temperatures of the range used (20–50°C) the reaction under air is slower than that under oxygen, but it is still not appreciably slowed by added triphenylphosphine This shows that the relative slowness of these reactions is not due to reversible dissociation of triphenylphosphine as a rate-determining step, and we propose this step to be homolytic fission of the Mn–Mn bond, followed by rapid reaction with oxygen of the $Mn(CO)_4PPh_3$ radicals so produced The activation parameters for the reaction with oxygen are $\Delta H^{\ddagger} = 28\ 8$ kcal/mole and $\Delta S^{\ddagger} = 19$ cal $mole^{-1}\ deg^{-1}$

Reaction with carbon monoxide proceeds at a limiting rate, under pressures of carbon monoxide from ca 20 mm up to 760 mm Hg, to form $Mn_2(CO)_9PPh_3$ $\Delta H^{\ddagger} = 28$ kcal $mole^{-1}$ and $\Delta S^{\ddagger} = 17$ cal $mole^{-1}\ deg^{-1}$ As with the corresponding reaction of $[Re(CO)_4PPh_3]_2$, this reaction is inhibited by added triphenylphosphine, but again this does not necessarily imply that dissociation of triphenylphosphine is the rate-determining step, and we choose to regard this also as a metal migration reaction At all temperatures studied this reaction is only about one half as fast as is that under oxygen If oxygen can react with the bridged intermediate (as has previously been concluded[3,5]) then the reaction with oxygen is proceeding both by the metal migration and homolytic fission paths The rough equality of the values of $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ for reaction with carbon monoxide and with oxygen shows that the homolytic fission and metal migration processes can occur with about equal facility. The fact that the reaction with carbon monoxide does not proceed as fast as with oxygen, coupled with the fact that no $Mn_2(CO)_{10}$ is formed, shows that dissociative loss of triphenylphosphine from $Mn(CO)_4PPh_3$ does not proceed at a rate competitive with the recombination of two $Mn(CO)_4PPh_3$ radicals

(iv) The reaction of $[Ru(CO)_4SiMe_3]_2$ with triphenylphosphine

This reaction proceeds cleanly in cyclohexane at 50–70°C to form equal amounts of $Ru(CO)_3(PPh_3)_2$ and $Ru(CO)_2(PPh_3)_2(SiMe_3)_2$ No intermediates are observed when the infrared spectrum is scanned during the reaction[14] The pseudo-first-order rate plots for loss of reactant carbonyl are linear for 1–2 half-lives, and the rate constants rise to a limiting value with increasing values of $[PPh_3]$. The reaction is retarded by carbon monoxide, but not to an extent compatible with the slower reactions (at lower $[PPh_3]$, and in the absence of added carbon monoxide) being retarded by carbon monoxide released during the reactions At pressures of carbon monoxide above about 100 mm of Hg, the relative amount of $Ru(CO)_3(PPh_3)_2$ increases until it is the sole product when p_{CO} is ca 300 mm, and the reaction is then very slow, although it does still go to completion The mechanistic implications of these results are not yet clear, but it may be that the reactive intermediate formed reversibly in the rate-determining step is again a carbonyl bridged species formed by metal migration (but see note added in proof, p 85)

C. DISCUSSION

The activation enthalpy for reactions of $MnRe(CO)_{10}$ is greater than that for reactions of $Mn_2(CO)_{10}$, and essentially equal to that for those of $Re_2(CO)_{10}$. This parallels the values of the force constants for the metal–metal vibrations which are 0.59, 0.81 and 0.82 mdyne/Å for the Mn–Mn, Mn–Re and Re–Re bonds, respectively[10]. Levenson et al.[15] have assigned the more intense band, of second to lowest energy, in the near UV region of the electronic spectrum of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ to a $\sigma \rightarrow \sigma^*$ transition involving orbitals in the metal–metal bond. The energy of this transition might be expected to provide some kind of estimate of the relative strengths of the metal–metal bonds. The energies of these transitions for $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$ are 29,100, 30,800 and 32,300 cm^{-1}, respectively, the value for the mixed carbonyl being roughly intermediate between the other two rather than closer to that of $Re_2(CO)_{10}$ as are the force constant and activation enthalpy. The values for the energies of the corresponding bands of $Mn_2(CO)_{10}$, $Mn_2(CO)_9PPh_3$ and $[Mn(CO)_4PPh_3]_2$ are 29,100, 28,500 and 25,600 cm^{-1}, respectively, which parallel the values of the activation enthalpies for what we assign to be metal migration processes, viz. 36.2, 34 (ref 16) and 28 kcal/mole, respectively. The energies for the corresponding bands for $Re_2(CO)_{10}$, $Re_2(CO)_9PPh_3$ and $[Re(CO)_4PPh_3]_2$ are 32,300, ca. 31,200 and 33,300 cm^{-1}, respectively, and thus again roughly parallels the activation enthalpies, viz. 38.6, 34.8 and 38.8 kcal/mole.

D. SUMMARY

These recent studies establish more cases of the reversible formation of reactive intermediates in reactions of a variety of metal–metal bonded carbonyls. In some cases positive evidence is available to discount simple reversible ligand dissociation as the process involved, and all cases but one are compatible with reversible metal migration, the exception being assignable to homolytic fission of the Mn–Mn bond in $[Mn(CO)_4PPh_3]_2$.

The metal migration hypothesis is consistent with the occurrence of the well known methyl migration process[9], with the existence of stable carbonyl bridges in a great many carbonyls, and with structural[1] and theoretical[13] evidence that a terminal carbon monoxide ligand on one metal is attracted to the other metal in the metal–metal bond to some degree, even in the undisturbed reactant complex. In addition, this formulation of the nature of the reactive intermediates provides a simple and satisfying way of explaining reactions such as that of $Mn_2(CO)_{10}$ with iodine to form $Mn(CO)_5I$ (ref. 3) and of $[Co(CO)_3PBu_3]_2$ with $SnCl_2$, in which the tin atom is inserted cleanly into the Co–Co bond[6]. In cases where independent evidence exists for the relative strengths of the metal–metal bonds, a reasonably good correlation is found between these and the corresponding activation enthalpies assigned to metal migration.

Note added in proof

We have recently found that, at high concentrations of complex, reaction (*iv*) becomes half order in [complex] and it appears, therefore, that reversible dissociation into two radicals may be the first rate-determining step Similar results have also been found for the reaction of $Mn_2(CO)_{10}$ with oxygen, and reversible homolytic fission of the metal–metal bond may be occurring here as well.

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