Scrambling Equilibria of Some Dimetal Decacarbonyls

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Equilibrium constants in decalin for the scrambling reaction (i) have been measured at 170—190 °C and over a wide range of concentrations. At 190 °C the average of 35 values for K is 2.13 ± 0.02, and

$$[Mn_2(CO)_{10}] + [Re_2(CO)_{10}] \rightleftharpoons 2[MnRe(CO)_{10}] \qquad (i)$$

$\Delta H^\ominus$ and $\Delta S^\ominus$ are 34.4 ± 1.3 kJ mol^{-1} and 80.3 ± 2.5 J K^{-1} mol^{-1}, respectively. The possible significance of these values is discussed together with the relationship between the value of $\Delta H^\ominus$ and various estimates of the absolute strengths of the individual metal–metal bonds.

Measurement of the relative or absolute strengths of metal–metal bonds in dinuclear carbonyls has remained a difficult problem ever since the first unsupported metal–metal bond was characterized in dimanganese decacarbonyl in 1957.[1] Direct quantitative measurement of homolysis equilibria in solution appears to have proved possible only for the complexes $[\{Fe(\eta^3\text{-}C_3H_5)(CO)_2L\}_2]$ (L = CO or P-donor ligand)[2] and $[Co_2(CO)_8]$.[3] We have studied the scrambling equilibrium (1) over a range of temperatures in decalin so as to obtain values for the relative heat contents of the molecules involved.

$$[Mn_2(CO)_{10}] + [Re_2(CO)_{10}] \rightleftharpoons 2[MnRe(CO)_{10}] \quad (1)$$

Experimental

The complexes $[Mn_2(CO)_{10}]$ (Strem Chemicals, Inc.) and $[Re_2(CO)_{10}]$ (Alpha Inorganics) were used as received. Decalin (Aldrich) was distilled under reduced pressure several times until the tetralin impurity was reduced to negligible levels as evidenced by the absence of absorption bands at 268 and 274 nm. It was then stored over molecular sieves. Reactions were carried out in Schlenk tubes after thorough degassing by several freeze–pump–thaw cycles and subsequent saturation of the solutions with appropriate gases [carbon monoxide and CO–N_2 gas mixtures (Matheson Canada, Ltd.): N_2 from Canox, Ltd.]. The Schlenk tubes were fitted with rubber septum caps, wrapped in aluminium foil, and immersed in an oil-bath thermostatted to within ±0.1 °C. Temperatures were measured with a precision thermometer immersed in an equivalent volume of solvent in a Schlenk tube placed in the same position in the oil-bath as the tube containing the reacting solutions. The course of the reactions was monitored by removing samples with a syringe fitted with a stainless steel needle, cooling them rapidly, and measuring their i.r. spectra at room temperature (*ca.* 25 °C) with a Perkin-Elmer 337 or Pye-Unicam SP3-200 spectrophotometer in cells fitted with KBr windows and having a pathlength of 1.0 mm. The initial concentrations of the solutions were controlled by mixing stock solutions of $[Mn_2(CO)_{10}]$ and $[Re_2(CO)_{10}]$. The stock solutions and mixtures prepared from them were shown to obey Beer's law at room temperature over the appropriate range of concentrations.

The formation of $[MnRe(CO)_{10}]$ was evidenced by the growth of the appropriate bands in the i.r. spectra[4] and by carrying out a reaction of $[Re_2(CO)_{10}]$ with a large excess of $[Mn_2(CO)_{10}]$ until virtually all the $[Re_2(CO)_{10}]$ had reacted. The excess of $[Mn_2(CO)_{10}]$ was removed by its decomposition under O_2 at 130 °C and the product solution, after filtration, showed i.r. bands in the ranges 400—750 and 1 800—2 300 cm^{-1} exactly as expected for $[MnRe(CO)_{10}]$.[4] The solutions also showed an absorbance maximum at 324 nm as expected.[5] After deoxygenation of the solution the product was found to undergo reaction at 140 °C with an excess of PPh_3 according to a first-order rate constant of 2.43 × 10^{-4} s^{-1} in excellent agreement with results obtained from conventionally prepared $[MnRe(CO)_{10}]$.[6]

As the reaction proceeded the bands due to $[Re_2(CO)_{10}]$ and $[Mn_2(CO)_{10}]$ decreased in intensity while those due to $[MnRe(CO)_{10}]$ grew until an equilibrium was attained. No other bands were observed. Apart from traces of oxygen, tetralin impurity in the decalin also led to instability in the equilibrium mixtures. This was evidenced by selective decomposition of the $[Mn_2(CO)_{10}]$ and an increase in the absorbance due to $[Re_2(CO)_{10}]$ according to a shift of equilibrium (1) from right to left. Data were, therefore, always rejected when the absorbance due to $[Re_2(CO)_{10}]$ showed any signs of increasing after the initial decrease. The values of the dimensionless equilibrium constants were calculated from the absorbances (measured at room temperature) of the clearly separated band due to $[Re_2(CO)_{10}]$ at 2 070 cm^{-1} by assuming the stoicheiometry shown in equation (1). The sampling technique was very much more rapid than the rate of adjustment of the equilibria on cooling the samples, so these absorbances are a good measure of the concentration of $[Re_2(CO)_{10}]$ in the equilibrium mixtures at the higher temperatures.

Results and Discussion

Although the equilibrium was not found to be established at 130—140 °C[7] it is attained at convenient rates at 170—190 °C. The equilibrium mixtures are stable for as long as an hour at 190 °C after an approach to equilibrium lasting *ca.* 30—40 min. A summary of the results is shown in Table 1 where it can be seen that they are of high precision and consistency over a wide range of initial compositions and conditions. Although the rates of approach to equilibrium are affected by the presence of CO the equilibrium positions are not. That the equilibrium can be approached from both sides is shown by the last three values listed. The equilibrium was initially set up at 170 °C when 54.5% of the original $[Re_2(CO)_{10}]$ remained in equilibrium with the other carbonyls. On increasing the temperature to 190 °C the equilibrium adjusted itself over a period of *ca.* 1 h after which it remained constant for another 30 min with 48.0% of the original [$Re_2(CO)_{10}$] present. On reducing the temperature to 165 °C the equilibrium concentration of [$Re_2(CO)_{10}$] increased to 55.5% and remained unchanged for a further 30 min. The equilibrium constants corresponding to these compositions are in excellent agreement with those obtained from the other experiments.

The value of $\Delta H^\ominus$ for reaction (1) shows that the enthalpy of [$MnRe(CO)_{10}$], over this temperature range, is 17.2 ± 0.7 kJ mol^{-1} higher than the average enthalpy of the homonuclear complexes. Other values related to the strengths of these metal–metal bonds are shown in Table 2 and their most remarkable features are the uncertainty of their significance and their paucity.

Table 1. Equilibrium data for the scrambling reaction (1). Initial concentrations: 10^4[$Mn_2(CO)_{10}$] = 4.0—12.4, 10^4[$Re_2(CO)_{10}$] = 2.5—8.5 mol dm^{-3}; concentration of [$Mn_2(CO)_{10}$]/concentration of [$Re_2(CO)_{10}$] = 0.4—4.5. Concentration of [$Re_2(CO)_{10}$] at equilibrium = 30—60% initial concentration of [$Re_2(CO)_{10}$]

No. of independent measurements	Temp. (°C)	Atmosphere[a]	K	$\sigma(K)$[b] (%)
20	190.0	N_2	2.14 ± 0.03	5.8
12		5% CO	2.13 ± 0.02	3.2
1		15% CO	2.15	
1		40% CO	2.10	
1		70% CO	2.02	
10	180.0	0—40% CO	1.70 ± 0.02	3.7
9	170.0	0—15% CO	1.40 ± 0.02	4.7
1[c]	170.0	N_2	1.39	
	190.0	N_2	2.11	
	165.0	N_2	1.26[d]	

$\Delta H^\ominus = 34.4 \pm 1.3$ kJ mol^{-1},[e] $\Delta S^\ominus = 80.3 \pm 2.9$ J K^{-1} mol^{-1},[e] $\sigma(K) = 3.7\%$[e]

[a] Solutions equilibrated with N_2 or CO–N_2 gas mixtures. [b] All uncertainties are estimates of standard deviations corrected for the number of degrees of freedom so that 95% confidence limits can be obtained by doubling the listed uncertainties. $\sigma(K)$ is the standard deviation of an individual measurement of K obtained from $100\{\Sigma[(K_{obs.} - K_{av.})/K_{av.})]^2/(N-1)\}^{\frac{1}{2}}$ ($K_{obs.}$ is an individual observed value of K, $K_{av.}$ is the average value, and N is the number of measurements) and correction for the number of degrees of freedom. [c] All three measurements on one solution. [d] Value calculated from $\Delta H^\ominus$ and $\Delta S^\ominus$ was 1.27. [e] Estimated from least-squares analysis of temperature dependence of all the values of $K_{obs.}$ according to the equation $\ln K_{obs.} = -\Delta H^\ominus/\boldsymbol{R}T + \Delta S^\ominus/\boldsymbol{R}$. The relevant standard state is for reaction in decalin over the concentration and temperature ranges specified. The effect of changing concentrations is likely to be negligible, but there is likely to be a significant temperature dependence of $\Delta H^\ominus$ and $\Delta S^\ominus$ (as implied in the discussion) though not large enough to be apparent over the restricted temperature range used here.

The mass spectroscopic data depend on certain assumptions regarding the cross-sections for reaction of the components of the equilibria with electrons and the electron impact data suffer from other ambiguities.[8] The thermochemical values were obtained by assuming that the M–CO bond strength is 1.5 times the M–M bond strength in each case.[9] Even a 1% error in the estimate of the M–CO bond strength leads to a 15% error in the M–M bond strength. The value for [$Mn_2(CO)_{10}$] is quite unreasonably low in view of its kinetic behaviour.[8,10] It has recently been shown [7,11] quite conclusively that none of the decacarbonyls involved in reaction (1) undergoes substitution by rate-determining and reversible homolytic fission of the metal–metal bonds as has been believed.[12,13] A detailed study of the kinetics of reaction (1) has now been reported.[14] The values of $\Delta H^\ddagger$ previously assigned to homolytic fission must now be recognized as lower limits (Table 2). If the value of 67 kJ mol^{-1} for the Mn–Mn bond strength is accepted then a value of $\Delta S^\ddagger$ for homolytic fission ($\Delta S_{hf}^\ddagger$) of *less than* −160 J K^{-1} mol^{-1} is implied.[13] Put in another way, if $\Delta S_{hf}^\ddagger$ is assigned a more reasonable value [5,15] of + 80 J K^{-1} mol^{-1} then a value of $\Delta H_{hf}^\ddagger$ of 67 kJ mol^{-1} would lead to a half-life for substitution or decomposition in air-equilibrated solutions at room temperature of a few microseconds as compared with a value of *ca.* 300 years obtained by extrapolation of the temperature dependence of rates obtained at higher temperatures.[5] Even if the value of 94 kJ mol^{-1}, recently accepted [16] as a more reasonable value for the Mn–Mn bond strength, is taken as an estimate of $\Delta H_{hf}^\ddagger$ this would still imply a half-life of only 150 ms for [$Mn_2(CO)_{10}$] in solution at room temperature. As a predictor of rate behaviour the thermochemical values for the Mn–Mn bond strength leave something to be desired, as do the values obtained by mass spectroscopy and electron impact methods also. The value of 128 kJ mol^{-1} for the Re–Re bond would require a value more negative than *ca.* −38 J K^{-1} mol^{-1} for $\Delta S_{hf}^\ddagger$ and is most probably at least 40 kJ mol^{-1} too low. The only way in which low values could have any validity is if the radicals formed by homolytic fission have an activation enthalpy for recombination of $\gtrsim$40—50 kJ mol^{-1}.[8] In view of the very high rate constants for dimerization of the [$Mn(CO)_5$] [17-19] and [$Re(CO)_5$] [19,20] radicals, and of the temperature independence of dimerization of [$Mn(CO)_5$],[17] this can be ruled as most unlikely.

The difference between the enthalpy of the mixed-metal complex [$MnRe(CO)_{10}$] and the average enthalpy of the

Table 2. Estimates of metal–metal bond strengths (kJ mol^{-1})

	[$Mn_2(CO)_{10}$]	[$MnRe(CO)_{10}$]	[$Re_2(CO)_{10}$]	Method	Ref.
ΔH[a]	104 ± 8			Mass spectrometry	*b*
D(M–M)[d]	105	210	187	Electron impact	*c*
M[e]	67	80[f]	128	Thermochemistry	9
$\Delta H_{hf}^\ddagger$[g]	$\geqslant$154	$\geqslant$163	$\geqslant$166	Kinetics	5
$\Delta H_D^\ominus$[h]	1 068	1 532[f]	2 029	Thermochemistry	9

[a] From equilibrium constants for homolysis in the gas phase at 210—310 °C. [b] D. R. Bidinosti and N. S. McIntyre, *Can. J. Chem.*, 1970, **48**, 493. [c] H. J. Svec and G. A. Junk, *J. Chem. Soc. A*, 1970, 2102. [d] Homolytic dissociation energies from the difference between the appearance potentials (the potential at which the ions become detectable in the mass spectrometer) of [$M(CO)_5$]$^+$ formed from [$M_2(CO)_{10}$] and [$M(CO)_5$]. The ionization potential of [$Re(CO)_5$] was assumed to differ from that of [$Mn(CO)_5$] to the same extent as the ionization potentials of [$Re(CO)_5X$] differ from those of [$Mn(CO)_5X$] (X = Cl, Br, or I). [e] Metal–metal bond energies calculated by dividing the enthalpy of total disruption of the molecule in the gas phase, $\Delta H_D^\ominus$, according to the assumption that the metal–metal bond strength is 68% that of the M–CO bond strength. This in turn is based on the assumption that M–CO bond strengths are independent of the nuclearity of the compound {*e.g.* the Fe–CO bond strength is the same in [$Fe(CO)_5$], [$Fe_2(CO)_9$], and [$Fe_3(CO)_{12}$]}. [f] Estimated from data in ref. 9 for [$Mn_2(CO)_{10}$] and [$Re_2(CO)_{10}$] combined with our value for $\Delta H^\ominus$ for reaction (1). [g] Lower limits of activation enthalpies for homolytic fission. [h] Enthalpy of total disruption of the molecule in the gas phase.

homonuclear complexes is 17 kJ mol^{-1}, *i.e.* positive and quite small. This is in sharp contrast to the value of -64 kJ mol^{-1} given by the electron impact data. While the values of the bond enthalpies obtained from the kinetics are only lower limits they do suggest rather small enthalpy differences between the complexes unless the values of $\Delta H_{hf}^{\ddagger}$ differ from the values of $\Delta H^{\ddagger}$ for substitution by rather different amounts for each complex. It may also be significant that the value of the Mn–Re interaction energy as defined by the energy of the $\sigma \longrightarrow \sigma^*$ transition is very close to the average of those for the homonuclear complexes.[5]

Because the enthalpy change for reaction (1) is rather small it is not easy to rationalize it. However, it may be that the situation is best described by saying that [$Re_2(CO)_{10}$] is more stable than would be expected by a simple extrapolation of the enthalpies of [$Mn_2(CO)_{10}$] and [$MnRe(CO)_{10}$], *i.e.* there is a factor determining the stability of [$Re_2(CO)_{10}$] that is not available even in the mixed complex. This extra stabilization of [$Re_2(CO)_{10}$] would then amount to 34 kJ mol^{-1}. [$Re_2(CO)_{10}$] is believed to be more stabilized by metal–metal π-bonding than is [$Mn_2(CO)_{10}$][21] and, for this to be the deciding factor, this stabilization must not increase linearly along the series [$Mn_2(CO)_{10}$], [$MnRe(CO)_{10}$], and [$Re_2(CO)_{10}$].

The value of the entropy of [$MnRe(CO)_{10}$] is *ca.* 33 J K^{-1} mol^{-1} more positive than the average of those of [$Mn_2(CO)_{10}$] and [$Re_2(CO)_{10}$] after allowance for statistical effects. Both [$Mn_2(CO)_{10}$] and [$Re_2(CO)_{10}$] are believed to undergo changes from the staggered D_{4d} to the eclipsed D_{4h} structure in the solid state under the influence of high pressure[22] but more complex behaviour is shown by [$MnRe(CO)_{10}$].[23] All three decacarbonyls undergo similar solid-state changes at normal pressures and moderately elevated temperatures.[24] [$Re_2(CO)_{10}$] is reported to be eclipsed in the gas phase[25] under the same conditions as [$Mn_2(CO)_{10}$] is staggered.[26] This evidence raises the possibility that, under the conditions of our experiments, [$Mn_2(CO)_{10}$] is staggered, [$Re_2(CO)_{10}$] is eclipsed, and [$MnRe(CO)_{10}$] undergoes free rotation. The entropy associated with this free rotation could account, at least in part, for the value of $\Delta S^{\ominus}$. Further, if [$Re_2(CO)_{10}$] is indeed eclipsed another factor that could account for its 34 kJ mol^{-1} greater stability is the reportedly greater π-bonding to the axial CO ligands.[22]

In any case, the value of $\Delta H^{\ominus}$ for the scrambling reaction must be considered to be a better measure of the relative bond strengths in the complexes than any others that are available. Moreover, they lead to a relatively low stability of [$MnRe(CO)_{10}$], whereas all other values suggest it is relatively more stable. (This includes estimates of the metal–metal force constants[27] as well as the data in Table 2.)

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