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Preliminary communication

THERMAL HOMOLYTIC FISSION OF THE Mo—Mo BOND IN $(h^5\text{-}C_5H_5)_2Mo_2(CO)_6$

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Summary

Kinetic studies of reactions of the Mo—Mo bonded complex $(h^5\text{-}C_5H_5)_2\text{-}Mo_2(CO)_6$ in decalin show that it undergoes reversible homolytic fission and that the activation enthalpy required to break the Mo—Mo bond is 135.9 ± 2.2 kJ mol^{-1}.

The strengths of metal—metal bonds in a number of dimetal binary carbonyls have been determined by thermochemical [1], kinetic [2], and mass spectroscopic methods [3], and quite extensive studies on the effects of substituents on the kinetic strengths of the metal—metal bonds have been reported [4]. Values for the strengths of metal—metal bonds in organometallic complexes are very much scarcer however [1,5]. We report here a kinetic study that shows that the complex $Cp_2Mo_2(CO)_6$ ($Cp = h^5\text{-}C_5H_5$) undergoes reversible homolytic fission of its Mo—Mo bond so that a kinetic measure of its strength can be determined.

Reaction of the complex in decalin under oxygen leads to a kinetically, quite well behaved first order decomposition over the temperature range 70—135°C. The half times of reaction vary from 14 h to ca. 30 s. The rates of decomposition are not affected by variation of the composition of O_2/N_2 mixtures above the solutions (or being passed through the solutions) during the reaction over the range 5—100% O_2, nor are they affected when the proportion of CO in CO/O_2 mixtures above the solutions is varied from 0—95%. Decomposition under anaerobic conditions is very slow.

Reaction with $C_{16}H_{33}I$ at 135°C in thoroughly deoxygenated decalin leads to almost instantaneous formation of $CpMo(CO)_3I$ in high yield but the reaction is inhibited by small amounts of O_2. Under these conditions the reaction proceeds at the same rate as the reaction with O_2 alone but $CpMo(CO)_3I$ is still formed in high yield. As the temperature of the reaction with $C_{16}H_{33}I$ under a 5% O_2/N_2 mixture is decreased the yield of $CpMo(CO)_3I$ decreases and the proportion of decomposition increases. The rates remain the same as those with O_2 alone, however.

These results provide strong evidence that the complex undergoes homolytic fission such that further reaction of the metal-centred radicals can occur in the presence of suitable reactants but, in their absence, the Mo—Mo bond can be reformed [6]. In the case of reaction with $C_{16}H_{33}I$ some sort of chain reaction seems to occur unless O_2 is also present to prevent it. A likely sequence of reactions is shown in equations 1—7. Reaction with O_2 alone is accounted for by equations 1 and 2, the latter being so fast that it overwhelms the reverse

$$Cp_2Mo_2(CO)_6 \rightleftharpoons 2\ CpMo(CO)_3\cdot \qquad (1)$$

$$CpMo(CO)_3\cdot + O_2 \rightarrow \text{decomposition} \qquad (2)$$

$$CpMo(CO)_3\cdot + RI \rightarrow CpMo(CO)_3I + R\cdot \qquad (3)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (4)$$

$$R\cdot + Cp_2Mo_2(CO)_6 \rightarrow \{R^- \ Cp_2Mo_2(CO)_6{}^{+\cdot}\} \qquad (5)$$

$$\{R^- \ Cp_2Mo_2(CO)_6{}^{+\cdot}\} \rightarrow CpMo(CO)_3R + CpMo(CO)_3\cdot \qquad (6)$$

$$CpMo(CO)_3R \rightarrow R\cdot + CpMo(CO)_3\cdot \qquad (7)$$

of 1 and leaves homolytic fission as the rate-determining step. Reaction with $C_{16}H_{33}I$ in the presence of O_2 is accounted for by reactions 1—4. The rate is still governed by the rate of homolytic fission but the nature of the products is governed by the relative rates of 2 and 3. Reaction 3 must be faster at higher temperatures where $CpMo(CO)_3I$ is the major product. However, the activation energy of 3 must be higher than that of 2 since decomposition becomes more pronounced as the temperature is decreased. The $R\cdot$ radicals are scavenged by reaction 4 and prevented from further participation in the reaction. Reactions 5—7 are postulated as one way of accounting for the very rapid reaction with $C_{16}H_{33}I$ in the absence of O_2. Reaction 5 must compete successfully with dimerization of $R\cdot$. Reaction 7 is suggested because no $CpMo(CO)_3R$ is found as a product. Although these reactions are not improbable further work would be necessary to elucidate this aspect of the system. Finally, the data suggest that no reversible CO dissociative steps are involved in any of these reactions.

The Eyring plot, based on rate constants for loss of complex by the homolytic fission process, is shown in Fig. 1 and leads to the values $\Delta H^{\neq}_{\mathrm{hf}} = 135.9 \pm 2.2$ kJ mol^{-1} and $\Delta S^{\neq}_{\mathrm{hf}} = 56.2 \pm 5.6$ J K^{-1} mol^{-1}. The activation enthalpy is a measure of the energy needed to stretch the Mo—Mo bond to breaking point and is therefore, a good kinetic measure of the strength of the Mo—Mo bond. No comparable values are available for analogous Cr—Cr and W—W bonds. However, a value of $\Delta H^0 = 234.4 \pm 3.8$ kJ mol^{-1} has been obtained for the equilibrium (eq. 8) in the gas phase by mass spectrometry [7]. Since the

$$Cp_2W_2(CO)_6 \rightleftharpoons 2CpW(CO)_3\cdot \qquad (8)$$

reverse of this reaction is likely to have a negligible value of $\Delta H^{\neq}$ [8] the

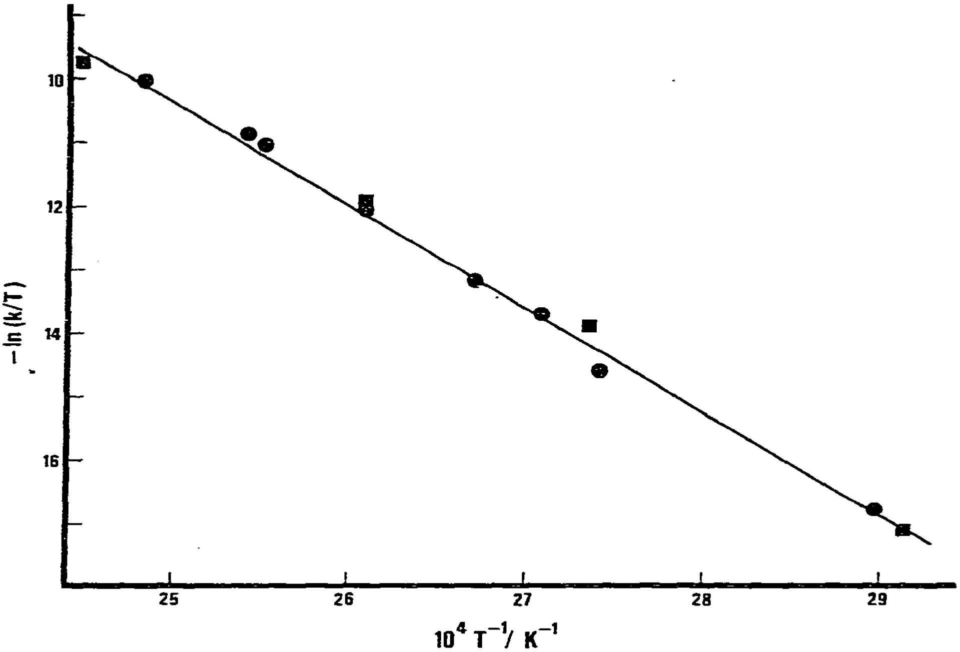

Fig. 1. Eyring plot homolytic fission reaction of $Cp_2Mo_2(CO)_6$ over the temperature range 70—135°C. ■: reaction with $C_{16}H_{33}I$; ●: reaction with O_2.

value 234.4 ± 3.8 kJ mol^{-1} may be taken as a fairly close measure of the activation energy for breaking the W—W bond. On the other hand it has been suggested that finite amounts of $CpCr(CO)_3$ are present in relatively labile equilibrium with $Cp_2Cr_2(CO)_6$ in solutions [9]. It appears, therefore, that the strength of the M—M bonds in $Cp_2M_2(CO)_6$ increase very much more rapidly with atomic weight of the metal than is the case for the bonds in $M_2(CO)_{10}$ (M_2 = Mn_2, Tc_2, and Re_2) [2,10]. This is likely to be due to steric effects [9];

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