Journal of Organometallic Chemistry, 51 (1973) C17–C20

Preliminary communication

Homolytic fission of metal–metal bonded carbonyls

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(Received December 12th, 1972; by publisher February 26th, 1973)

SUMMARY

Several reactions of metal–metal bonded carbonyls have been found to obey a rate law characteristic of reversible homolytic fission of the metal–metal bond as the first stage of the reaction.

Earlier kinetic studies[1-5] have led to the formulation of several mechanisms for the various reactions undergone by metal carbonyls that contain metal–metal bonds unsupported by carbonyl or other bridging groups. While it is quite likely that each of these mechanisms may be operative in particular cases, we now report detailed kinetic studies that provide strong evidence for reversible homolytic fission of the metal–metal bond as an initial step in several reactions.

Treatment of $[Mn(CO)_4PPh_3]_2$ with an excess of triphenylphosphine in cyclohexane at 50–70° has been shown[5] to give rate plots half order with respect to [complex], and to give a product tentatively assumed to be *cis*-$Mn(CO)_3(PPh_3)_2$. Unfortunately the limited solubility of the complex combined with its sensitivity to oxygen precludes a study of initial rates *vs.* [complex] but the analogous reaction of $[Mn(CO)_4P(OPh)_3]_2$ with tritriphenylphosphite at 117° shows the same sort of behaviour[6] and the initial rates show half-order dependence on [complex] over the range $(5 \text{ to } 70) \times 10^{-5}$ *M*. The reaction of $[Re(CO)_4PPh_3]_2$ with triphenylphosphine at 180° is also half-order in [complex] (over the concentration range $(4 \text{ to } 190) \times 10^{-5}$ *M*) and the product shows a well defined ESR spectrum and an IR spectrum characteristic[7] of $M(CO)_3L_2$ molecules. In all cases the rates are independent of [ligand] and the reactions probably proceed, therefore, by reversible homolytic fission to form small, steady-state concentrations of $M(CO)_4L$ radicals that are then further substituted by a dissociative process. The rate law for a reaction:

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$$A_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2A; \quad A \xrightarrow{k_2} \text{products}$$

is given by equation (1). At high values of $k_1 k_{-1} [A_2]/k_2^{\,2}$ the rate approaches 0.5 $k_2(k_1/k_{-1})^{1/2}[A_2]^{1/2}$.

$$-\,d[A_2]/dt = R = \{k_2^{\,2}/8k_{-1}\}\,\{(16k_1k_{-1}[A_2]/k_2^{\,2} + 1)^{1/2} - 1\} \qquad (1)$$

Decomposition of manganese carbonyl in decalin at 155° under argon shows initial rates that are half-order in $[Mn_2(CO)_{10}]$ over the range (2.5 to 300) × 10^{-5} *M*. No carbonyl containing products are observed and the products appear simply to be finely divided manganese metal and carbon monoxide. The half-order rate plots show gradients that increase over the last 40% reaction, behaviour consistent with some autocatalysis by finely divided metal product[1]. At temperatures below ca. 140° the decomposition is not retarded when the atmosphere of argon is replaced by carbon monoxide so the slowness of the decomposition under argon compared with substitution and other reactions cannot be due to inhibition by carbon monoxide released during the reaction. Decomposition under air to non-carbonyl-containing products (presumably manganese oxides) is much faster and is first-order in [complex] at 1 × 10^{-5} *M*-complex but decreases almost to half-order by 300 × 10^{-5} *M*. If the mechanism of this reaction is assumed to be

$$[Mn(CO)_5]_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,Mn(CO)_5\,;\, Mn(CO)_5 \xrightarrow[k_2]{O_2} \text{products},$$

where k_2 is now a bimolecular rate constant for the reaction of $Mn(CO)_5$ radicals with oxygen, then the rate law should be given by equation (1) in which k_2 is replaced by $k_2\,[O_2]$. As $[A_2]$ is increased, or as $[O_2]$ is decreased, the rate should change from a first- to a half-order dependence on $[Mn_2(CO)_{10}]$, the limiting rate at low $[Mn_2(CO)_{10}]$ and/or high $[O_2]$ being $k_1\,[Mn_2(CO)_{10}]$. Equation (1) can be rearranged to give (2) where $R_1 = k_1\,[A_2]$,

$$R_1/R = 1 + 4k_{-1}R/k_2^{\,2}\,[O_2]^2 \qquad (2)$$

and R is the observed initial rate at the same concentration of complex. A plot of R_1/R *vs.* $R/(p(O_2))^2$ for reactions at 125° is shown in Fig.1 where $p(O_2)$ varies from 5.1 to 44.8 cm Hg at $[Mn_2(CO)_{10}] = 2.9 \times 10^{-4}$ *M*, and $[Mn_2(CO)_{10}]$ varies from (1 to 300) × 10^{-5} *M* at $p(O_2) = 15.8$ cm Hg. R_1 is obtained from limiting rates at high $p(O_2)$ and relatively low $[Mn_2(CO)_{10}]$ where the rates are simply first order in $[Mn_2(CO)_{10}]$. The diagonal lines correspond to an uncertainty of ±20% in the values of R and suggest a not unreasonable standard of deviation of ca. ±10% for an individual measurement of R. A value of $(6.6 \pm 0.7) \times 10^8\ l\cdot mol^{-1}\cdot(cm\ Hg)^2\cdot s$ is obtained for $k_{-1}/k_2^{\,2}$. No retardation of the decomposition was observed when a N_2–O_2 atmosphere above the reactant solution was replaced by a CO–O_2 mixture. Less extensive studies on the decomposition of $MnRe(CO)_{10}$ in the presence of various amounts of oxygen appear to show the same behaviour.

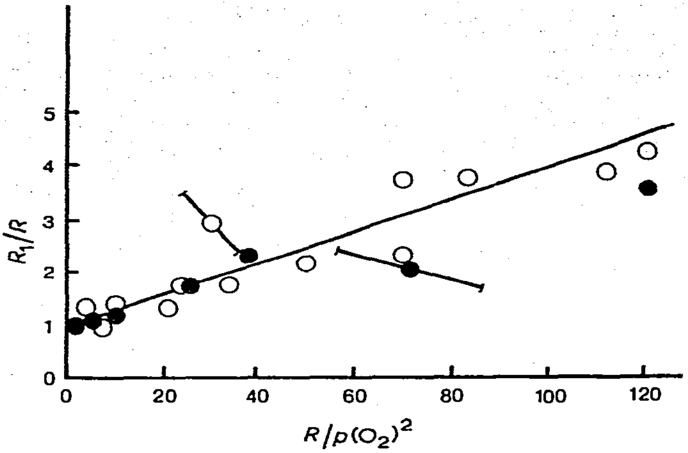

Fig.1. Decomposition of manganese decacarbonyl under oxygen at 125°. •, $[Mn_2(CO)_{10}]$ = 2.87×10^{-4} *M*, $p(O_2)$ = variable; ○, $p(O_2)$ = 15.8 cm Hg, $[Mn_2(CO)_{10}]$ = variable. Rates in mol•l^{-1}•s^{-1}; $p(O_2)$ in cm Hg.

Further study[5] of the reaction[8] of $[Ru(CO)_4SiMe_3]_2$ with triphenylphosphine in cyclohexane, to form equivalent amounts of $Ru(CO)_3(PPh_3)_2$ and $Ru(CO)_2(PPh_3)_2(SiMe_3)_2$, shows that initial rates change steadily from a first-order towards a half-order dependence on [complex] as [complex] is increased from (6 to 400) × 10^{-6} *M*. Reactions with bromotrichloromethane result in IR spectral changes expected for initial formation of $(Me_3Si)Ru(CO)_4Br$ [9]. These reactions were not kinetically well behaved but the rates were about equal to, or somewhat greater than, the limiting first order rates with triphenylphosphine. These results are again suggestive of reversible homolytic fission although the overall reaction is considerably more complex than the others studied here and further study is in progress.

The results reported here provide, therefore, several examples of reactions whose kinetic pattern fits very well with reversible homolytic fission of the metal–metal bond as the initial step, subsequent steps depending on the nature of the overall reaction. Limiting rates of such reactions should provide rate parameters characteristic of the strengths of the metal–metal bonds involved.

ACKNOWLEDGEMENTS

We thank Erindale College and the National Research Council of Canada for support.

REFERENCES

1 L.I.B. Haines, D. Hopgood and A.J. Poë, *J. Chem. Soc. (A)*, (1968) 421.
2 P.F. Barrett and A.J. Poë, *J. Chem. Soc. (A)*, (1968) 429.
3 L.I.B. Haines and A.J. Poë, *J. Chem. Soc. (A)*, (1969) 2286.

4 F. Basolo and H. Wawersik, *Inorg. Chim. Acta*, 3 (1969) 113.
5 D. DeWit, J.P. Fawcett, A.J. Poë, and M.V. Twigg, *Coordin. Chem. Rev.*, 8 (1972) 81.
6 D.M. Chowdhury and A.J. Poë, unpublished work.
7 M. Freni, D. Giusto and P. Romiti, *J. Inorg. Nucl. Chem.*, 29 (1967) 761; H. Nakayama, *Bull. Chem. Soc. Japan*, 43 (1970) 2057.
8 S.A.R. Knox and F.G.A. Stone, *J. Chem. Soc. (A)*, (1969) 2559.
9 M.J. Ash, A. Brookes, S.A.R. Knox and F.G.A. Stone, *J. Chem. Soc. (A)*, (1971) 458.