Kinetics of Reactions of Bromine and Iodine with Some Substituted Dimanganese and Dirhenium Carbonyls†

By Gary Kramer, Lily Ng, and Anthony Poë*

(*Erindale College and the Department of Chemistry, University of Toronto, Mississauga, Ontario* L5L 1C6, *Canada*)

Summary Kinetic studies show that reactions of Br_2 and I_2 with several substituted dimanganese and dirhenium carbonyls occur *via* very rapid initial formation of intermediate adducts containing one or more halogen molecules; the dependence of the rates on the nature of the substituents is consistent with electrophilic attack by halogen at the extremity of the carbonyl ligands.

Reactions of X_2 (X = Br or I) with the complexes shown in the Table proceed rapidly in cyclohexane or decalin to form *cis*-$[Mn(CO)_4XL]$ and, sometimes, the *trans* isomer as well. They have been followed by the stopped-flow technique and are first-order in [complex]. Orders >1 in $[X_2]$ are frequently shown and suggest a sequence of fast, reversible formations of X_2-complex adducts. This is supported by very rapid initial spectroscopic changes, some negative temperature coefficients and, in two cases, a rate equation $k_{obs} = a[X_2]^2/(1 + b[X_2])$ (k_{obs} is an observed pseudo-first-order rate constant and a and b are constants). The latter shows that terms first-order in $[X_2]$ could result from rapid and complete formation of a 1:1 adduct followed by slow bimolecular reaction of the

Table

Rate constants[a] for reaction of bromine and/or iodine with $[M_2(CO)_{10-n}L_n]$ in cyclohexane or decalin at 25 °C

Complex			Reaction with bromine		Reaction with iodine	
M	L_n	ν_{CO}[b]/cm^{-1}	k_2/dm^3 mol^{-1} s^{-1}	k_3/dm^6 mol^{-2} s^{-1}	k_3/dm^6 mol^{-2} s^{-1}	k_4/dm^9 mol^{-3} s^{-1}
Re	$(PPh_3)_2$	1965	$3{\cdot}34 \times 10^4$		$1{\cdot}23 \times 10^5$	
Re	$(PPh_3)_1$	1998		$1{\cdot}70 \times 10^4$	$23{\cdot}2$	$5{\cdot}82 \times 10^3$
Re	$(CO)_1$	2015			5×10^{-6}[c,d]	
Mn	$(PBu_3)_2$	1948	$2{\cdot}16 \times 10^3$		$9{\cdot}39 \times 10^4$	
Mn	$(PEt_3)_2$	1950	$7{\cdot}97 \times 10^2$		$2{\cdot}50 \times 10^4$	
Mn	$(PEt_2Ph)_2$	1952	$1{\cdot}44 \times 10^3$		$1{\cdot}05 \times 10^5$	
Mn	$(PEtPh_2)_2$	1956	$1{\cdot}42 \times 10^2$	$7{\cdot}37 \times 10^3$		
Mn	$(PPh_3)_2$	1960		$1{\cdot}61 \times 10^4$	$0{\cdot}4$[c]	$5{\cdot}5 \times 10^5$
Mn	$\{P(OMe)_3\}_2$	1967	$17{\cdot}9$	$7{\cdot}85 \times 10^3$		
Mn	$\{P(OPh)_3\}_2$	1983	$2{\cdot}03$	$4{\cdot}25 \times 10^2$	$9{\cdot}1$	$1{\cdot}69 \times 10^2$
Mn	$(PPh_3)_1$	1997	$1{\cdot}07$	$4{\cdot}65 \times 10^2$ [e]		
Mn	$(CO)_1$	2015			2×10^{-8}[c,f]	

[a] Rates are first order in [complex] and first order (k_2), second order (k_3), and third order (k_4) in $[X_2]$. [b] Frequency of the most intense band in C–O stretching region for the complex. [c] k_2. [d] Calc. from data in ref. 4. [e] k_4. [f] Calc. from data in ref. 3.

---

† No reprints available.

adduct with another halogen molecule. Zero orders could be obtained if the adduct underwent unimolecular reaction.[1] An order greater than unity has been observed[2] for reaction of I_2 with $[Fe(\eta^5\text{-}C_5H_5)(CO)_2(SnMe_3)]$ but not, it appears, in reactions of other metal carbonyls.[3-6] They are known for reactions with some tin complexes[7] and with unsaturated hydrocarbons.[8]

Reactions with the substituted carbonyls are all very much faster than with the decacarbonyls.[3,4] Similarly pronounced labilization by As-[5] or P-donor[9] substituents has been found previously in a few cases. Within a series of substituted carbonyls the rate constants vary by several orders of magnitude and corresponding rate constants tend to decrease with increasing frequency of the main C–O stretching band. A roughly linear decrease of log k_2, for reaction of Br_2 with $[\{Mn(CO)_4L\}_2]$, with increasing Δ(h.n.p.)‡ of L is shown; this behaviour is similar to that found for oxidation potentials of substituted dicobalt carbonyls.[10] Apart from this, no dependence on the detailed nature of the substituents is obvious, nor does the ease of breaking the Mn–Mn bonds[11] affect the rate sequence.

These results (Table) show that the rates increase with increasing electron density at the extremity of the carbonyl ligands, and are consistent with electrophilic attack by halogen in that region of the complexes. In view of the sterically crowded nature of the complexes it seems unlikely that attack occurs directly at the metal.

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

(*Received*, 21*st January* 1977; *Com.* 049.)

---

‡ The relative half neutralisation potential (h.n.p.) for titration of L with perchloric acid in nitromethane (F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 572).

[1] J. P. Candlin and J. Cooper, *J. Organometallic Chem.*, 1968, **15**, 230.
[2] J. R. Chipperfield, J. Ford, A. C. Hayter, and D. E. Webster, *J.C.S. Dalton*, 1976, 360.
[3] L. I. B. Haines, D. J. Hopgood, and A. J. Poë, *J. Chem. Soc.* (*A*), 1968, 421.
[4] L. I. B. Haines and A. J. Poë, *J. Chem. Soc.* (*A*), 1969, 2826.
[5] W. R. Cullen and F. L. Hon, *Inorg Chem*, 1975, **14**, 3121.
[6] J. R. Chipperfield, J. Ford, A. C. Hayter, D. J. Lee, and D. E. Webster, *J. C. S. Dalton*, 1976, 1024.
[7] G. Martino and J.-C. Jungers, *Bull. Soc. chim. France*, 1970, 3392.
[8] K. Yates, R. S. McDonald, and S. A. Shapiro, *J. Org. Chem.*, 1973, **38**, 2460.
[9] D. G. DeWit, J. P. Fawcett, and A. J. Poë, *J.C.S. Dalton*, 1976, 528.
[10] D. de Montauzon and R. Poilblanc, *J. Organometallic Chem.*, 1976, **104**, 99.
[11] J. P. Fawcett, A. J. Poë, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1973, 267; R. A. Jackson and A. J. Poë, *Proc.* 16*th Internat. Conf. Co-ordination Chem.*, Dublin, 1974, paper 3·20.