Reaction Mechanisms of Metal–Metal-bonded Carbonyls. Part 21.[1] Reactions of Bromine with Some Substituted Binuclear Carbonyls [2]

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The kinetics have been followed of reactions of bromine in cyclohexane or decalin with a number of axially substituted complexes $[M_2(CO)_{10-n}L_n]$ (M_2 = Mn_2, MnRe, or Re_2; n = 1 or 2; L = phosphorus-donor ligand). The reactions are fast and the major products are the complexes *cis*-$[M(CO)_{5-m}BrL_m]$ (m = 0 or 1). Orders as high as three in $[Br_2]$ are observed and there is kinetic evidence for very rapid pre-association of Br_2 with $[Mn_2(CO)_8(PEt_2Ph)_2]$ before the relatively much slower oxidation step. Reaction of $[Mn_2(CO)_8\{P(OMe)_3\}_2]$ in other solvents shows similar evidence. The rates of oxidation of $[M_2(CO)_8(PPh_3)_2]$ (M_2 = Mn_2, MnRe, or Re_2) show a close inverse relationship to their ease of polarographic reduction. Rates of oxidation of the dimanganese complex generally increase with the basicity of the substituents although the bis(tricyclohexylphosphine) and, probably, the bis(triphenylphosphine) complexes show evidence of steric retardation. The data are all consistent with initial electrophilic attachment of one or more Br_2 molecules at O atoms of the carbonyl ligands. The subsequent steps are not defined by the kinetics. The effects of using MeOH, CH_2Cl_2, and CCl_4 as solvents were also examined. The rate equations changed and their form shows evidence for formation of $[Mn_2(CO)_8\{P(OMe)_3\}_2(Br_2)]$ and $[Mn_2(CO)_8\{P(OMe)_3\}_2(Br_2)_2]$ adducts in MeOH, and of only the former in CH_2Cl_2 and CCl_4. Overall rates are much increased but no simple rationalization is possible.

REACTIONS of halogens with polynuclear metal carbonyls can be used to prepare mononuclear halogenocarbonyls in high yields [3] yet very few studies of the mechanisms of such reactions have been reported. Haines *et al.*[4] described a slow reaction between iodine and $[Mn_2(CO)_{10}]$ in decalin that was first order in the concentration of each reactant, and a similar reaction between I_2 and $[Re_2(CO)_{10}]$ was reported later.[5] Candlin and Cooper [6] reported [halogen]-independent reactions of Cl_2 and Br_2 with $[Os_3(CO)_{12}]$ and there was evidence of rapid formation of a cluster–halogen complex before the relatively slow formation of the ring-opened product $[X\{Os(CO)_3\}_3X]$. More recently Cullen and Hou [7] have described $[I_2]$-dependent reactions of some $[M_2(CO)_8(L\text{–}L)]$ complexes ($M_2 = Mn_2$, MnRe, or Re_2; L = a chelating *As*-donor ligand co-ordinated at an equatorial position on each metal atom). The reactions involve formation of two mononuclear iodocarbonyl species linked through the chelate and are very much faster than those of the unsubstituted carbonyls. Substitution of two PPh_3 ligands into $[Re_2(CO)_{10}]$ also greatly increases the rate of reaction with I_2, the substituted complex reacting very rapidly at room temperature [8] while the unsubstituted one reacts [5] slowly at 100 °C.

In view of the pronounced labilizing effects of *As*- and *P*-donor ligands we have begun a systematic study of the reactions of substituted polynuclear metal carbonyls in an attempt to elucidate the factors governing their rates and define the mechanisms involved. We report here the results of a kinetic study of reactions of Br_2 with some axially substituted $[M_2(CO)_{10-n}L_n]$ complexes ($M_2 = Mn_2$, MnRe, or Re_2; L = *P*-donor ligand; n = 1 or 2).

EXPERIMENTAL

Reagents.—The preparation of the complexes has been described elsewhere.[9] Bromine (Baker Analysed Reagent) was used as received, and decalin (Baker Analysed Reagent) and cyclohexane (AnalaR, B.D.H. Ltd.) were dried over molecular sieves and used without further purification. Argon (99.998%, Linde specialty gases) was obtained from Union Carbide of Canada, Ltd.

Products.—The reactions were accompanied by complete loss of the electronic and i.r. absorptions characteristic of the metal–metal-bonded complexes [9,10] and the appearance of i.r. bands in the C–O stretching region that can be ascribed to *cis*-$[M(CO)_4Br(L)]$ products.[11] Other bands or shoulders attributable to the formation of *trans* isomers [11] were usually observed as well. Thus the reaction products from $[Mn_2(CO)_8(PPh_3)_2]$ showed i.r. bands at 2 085s, 2 021s, 2 005vs, and 1 959s cm^{-1} characteristic of *cis*-$[Mn(CO)_4Br(PPh_3)]$, and a shoulder at 1 986 cm^{-1} characteristic of the *trans* isomer.[11] Products from $[Re_2(CO)_8(PPh_3)_2]$ had bands at 2 100s, 2 015s, 1 999vs, and 1 945s cm^{-1} due to the *cis* product and a shoulder at 1 990 cm^{-1} due to the *trans* product. Product bands from $[MnRe(CO)_8(PPh_3)_2]$ were at 2 105s, 2 090s, 2 023s, 2 005s, 1 996vs, 1 994 (sh), 1 960s, and 1 950s cm^{-1} which correlate well with those expected from a mixture of *cis*- and *trans*-$[Mn(CO)_4Br(PPh_3)]$ and -$[Re(CO)_4Br(PPh_3)]$. The *trans*-$[Mn(CO)_4Br(PPh_3)]$ was seen to change into the *cis* isomer with time at room temperature while the corresponding Re isomer remained unchanged under the same conditions.

The complexes $[Mn(CO)_5Br]$ and *cis*- and *trans*-$[Mn(CO)_4Br(PPh_3)]$ were the products of the reaction with $[Mn_2(CO)_9(PPh_3)]$. In no case was there any evidence for the presence of detectable amounts of other carbonyl-containing products or for oxidation products such as MBr_2. In preparative reactions [11] of $[M_2(CO)_8(PPh_3)_2]$ (M = Mn or Re) with Br_2 total yields of *cis* and *trans* products were *ca.* 80% in both cases even after chromatographic separation of the isomers. These reactions can, therefore, all be concluded to proceed to completion in essentially quantitative yields.

Kinetics.—Solutions of the complexes in cyclohexane or decalin were prepared when possible by simple dissolution of weighed samples in volumetric flasks. Complexes that were more difficult to dissolve in the hydrocarbons were dissolved initially in a little dichloromethane which was removed under reduced pressure after addition of hydrocarbon solvent. The complex $[Mn_2(CO)_8\{P(C_6H_{11})_3\}_2]$ is sensitive to aerial oxidation ($t_{\frac{1}{2}}$ *ca.* 20 min at 25 °C) [9] and solutions were prepared in a Schlenk tube, degassed by freeze–pump–thaw cycles, and stored under argon. Standard solutions of Br_2 were prepared immediately before use by dissolving known weights of Br_2 in the solvent in a volumetric flask and making up to the mark. All solutions were prepared in foil-wrapped flasks. Reactions were followed by monitoring the changing absorbance at the absorbance maximum in the near u.v. that is characteristic of all these metal–metal-bonded carbonyls.[9,10] Final absorbances were due only to unchanged Br_2 in various pseudo-first-order excesses.

Slower kinetic runs ($t_{\frac{1}{2}} > 15$ s) were followed in 10-mm silica cells in a Cary 16K spectrophotometer. The cell compartment was thermostatted at *ca.* 5 °C below the reaction temperature while the cell holder was thermostatted with a Lauda K-4/R circulator. Temperatures in the cell were measured with a Pt resistance thermometer (Minco Corp.) attached to a model 3500 digital multimeter (Data Precision Corp., resistance mode) and calibrated at the triple point of water. Temperatures were constant to within ± 0.1 °C. Solutions (2.7 cm^3) of Br_2 were thermostatted in the cells before rapid addition of 0.3 cm^3 of a solution of the complex. The cells were stoppered and shaken and returned to the cell holder within *ca.* 10 s. Reactions were followed by ' continuous-drive ' operation. Faster reactions were followed on a model SF-3A ' Canterbury ' stopped-flow spectrometer (Nortech Laboratories Ltd.) equipped with a model 805 waveform recorder (Biomation Corp.), a model OS 250 dual-trace oscilloscope (Advance Electronics Ltd.), and a model SR-20 4 strip-chart recorder (Heath Co.). The flow system was immersed in a thermostatted bath of ethylene glycol–water (1 : 1). Solutions were left in the flow system for at least 4 min for temperature equilibration. When reactions of $[Mn_2(CO)_8\{P(C_6H_{11})_3\}_2]$ were followed the space above the solutions in the reservoirs was filled with argon.

Solutions in the 0.2 mm pathlength observation-reaction cell always had absorbances of <0.2 (due to halogen) $+$ 0.13 (due to complex) so that transmittance was always $>45\%$. The change in transmittance was always $<20\%$. The dual time-base facility on the waveform recorder was used so that most of the 2 048 memory channels were used to record the first 70—90% of reaction while the remaining ones were used to record the final transmittance. The data in the recorder were displayed on the oscilloscope and at least two traces were obtained for a given solution to check reproducibility before a final run was performed and the trace drawn on the chart recorder. The trace is essentially one of voltage from the photomultiplier against time.

In all cases pseudo-first order excesses of Br_2 were present and simple plots of $\log(A_t - A_\infty)$ against time were used to obtain rate constants, $k_{obs.}$, for the reactions followed on the Cary spectrophotometer. Plots of $\log(V_\infty - V_t)$ against time were used to obtain values of $k_{obs.}$ from the stopped-flow traces (V = voltage, in arbitrary units, read from the traces). This is possible because a plot of absorbance against percentage transmittance (T) is observably linear over the ranges used in these experiments. For a change of absorbance from 0.33 to 0.20 the average deviation of absorbance from a linear least-squares plot of A against T is only 0.7%, and for smaller absorbance changes and/or smaller absolute absorbances the deviation is even smaller. Since the voltage output recorded on the chart is proportional to the transmittance, and the transmittance is proportional to the absorbance, we have $A = -\alpha V + \beta$ (α and β are constants) so that $\log(A_t - A_\infty) = \log(V_\infty - V_t) + \log \alpha$. Although α varies depending on the absorbance range being followed, the gradient of the dependence of $\log(V_\infty - V_t)$ on t will be related to $k_{obs.}$ in exactly the same way as the gradient of the plot of $\log(A_t - A_\infty)$ against time. Rate plots made in this way were linear for up to *ca.* 75% reaction. The pseudo-first-order rate constants for all reactions studied were found to depend on $[Br_2]$. Rate data were obtained over wide ranges of $[Br_2]$ and, usually, over substantial ranges of [complex]. Half-lives varied from *ca.* 5 ms to 50 s.

RESULTS

Reactions of Br_2 *with* $[Re_2(CO)_8(PPh_3)_2]$ *and* $[Mn_2(CO)_8L_2]$ ($L = PBu^n_3$, PEt_3, *or* PEt_2Ph). The first two reactions showed orders of 0.89 ± 0.07 and 1.01 ± 0.01 with respect to [complex] over 5- and 50-fold ranges of concentration, respectively. The other two reactions were assumed also to be first order in [complex]. The concentration of Br_2 was varied over a 25- to 60-fold range, *e.g.* 7×10^{-5}—450×10^{-5} mol dm^{-3} for the reaction of $[Mn_2(CO)_8(PBu_3)_2]$. All the reactions were first order in $[Br_2]$, plots of $k_{obs.}$ against $[Br_2]$ being linear with negligible intercepts. The results of a weighted least-squares fit of the data to $k_{obs.} = a + k_2[Br_2]$ are shown in Table 1. Values of $k_{obs.}$ were assumed to have a constant percentage standard deviation, $\sigma(k_{obs.})$. The reaction of $[Mn_2(CO)_8(PEt_2Ph)_2]$ became rather irreproducible above $[Br_2] = 3 \times 10^{-3}$ mol dm^{-3}, the scatter rising to $\pm 20\%$. Otherwise the values of $\sigma(k_{obs.})$ were $\leqslant 10\%$. Since values of a were negligible, plots of $k_{obs.}/[Br_2]$ against $[Br_2]$ were horizontal as shown in Figure 1.

TABLE 1

Rate constants [a] for the reactions of $[M_2(CO)_8L_2]$ with Br_2 according to the pseudo-first-order rate equation $k_{obs.} = a + k_2[Br_2]$

Complex	θ_c/°C	a/s^{-1}	$10^{-2}k_2$/dm^3 mol^{-1} s^{-1}	$\sigma(k_{obs.})$/%
$[Re_2(CO)_8(PPh_3)_2]$ [b]	25.0	-5.8 ± 1.0	373 ± 12	7.9
$[Mn_2(CO)_8(PBu_3)_2]$ [c]	25.2	$(3 \pm 16) \times 10^{-3}$	21.9 ± 1.3	9.8
$[Mn_2(CO)_8(PEt_3)_2]$ [c]	24.7	$-(4 \pm 1) \times 10^{-2}$	8.0 ± 0.3	10.0
$[Mn_2(CO)_8(PEt_2Ph)_2]$ [c]	24.9	$(11 \pm 1.3) \times 10^{-2}$	14.4 ± 0.3	5.4

[a] Uncertainties quoted throughout this paper are standard deviations that have been adjusted, according to the number of degrees of freedom, so that 95% confidence limits can be obtained by multiplying them by 1.96. [b] In decalin. [c] In cyclohexane.

Apart from the reaction of $[Mn_2(CO)_8(PEt_2Ph)_2]$, good fits of the data to the Eyring equation were obtained over the range 25—50 °C. $[Br_2]$ was generally varied over a three-fold range at each of four temperatures and values of k_2 were taken to be given by $k_{obs.}/[Br_2]$. A non-weighted linear least-squares analysis of the dependence of $\log(k_{obs.}/T)$ on $1/T$ led to the activation parameters shown in Table 3. The values of $\sigma(k_{obs.})$ obtained were close to the corresponding ones for the $[Br_2]$ variation at 25 °C. In the case of $[Mn_2(CO)_8(PEt_2Ph)_2]$, however, the Eyring plot was perceptibly concave with respect to the origin and $\sigma(k_{obs.})$ (19.4%) from the temperature dependence was much larger than that from the $[Br_2]$ dependence at 25 °C.

Reactions of Br_2 *with* $[MnRe(CO)_8(PPh_3)_2]$, $[Re_2(CO)_9$-

$(PPh_3)]$, *and* $[Mn_2(CO)_8L_2]$ [L = $PEtPh_2$, $P(OMe)_3$, $P(OPh)_3$, PPh_3, *or* $P(C_6H_{11})_3$].—When L = $P(OMe)_3$, PPh_3, and $P(C_6H_{11})_3$ the orders of the reactions with respect to [complex] are 1.09 ± 0.04, 0.95 ± 0.04, and 1.10 ± 0.06, respectively, over 14-, 20-, and 4-fold ranges of [complex]. For $[MnRe(CO)_8(PPh_3)_2]$ and $[Re_2(CO)_9(PPh_3)]$ they are 0.98 ± 0.03 and 1.02 ± 0.06, respectively, both for 10-fold ranges. The gradients of the plots of log $k_{obs.}$ against log$[Br_2]$ varied from 1.03 ± 0.03 for $[Mn_2(CO)_8(PEtPh_2)_2]$ to 1.98 ± 0.05 for $[Re_2(CO)_9(PPh_3)]$, the other complexes showing intermediate values. The data for these reactions were, therefore, analysed according to a linear least-squares fit to the equation $k_{obs.}/[Br_2] = k_2 + k_3[Br_2]$. Values of k_2 and k_3 are shown in Table 2 together with their standard deviations. Typical plots of $k_{obs.}/[Br_2]$ against $[Br_2]$ are shown in Figure 1. For L = $P(OMe)_3$ the rate constants became increasingly scattered at $[Br_2] = >3 \times 10^{-2}$ mol dm^{-3}, the spread of the values rising to *ca.* ±25%. At $<3 \times 10^{-2}$ mol dm^{-3} the data were quite reproducible and the least-squares analysis shows no systematic increase of the uncertainty in $k_{obs.}$ with increasing $[Br_2]$.

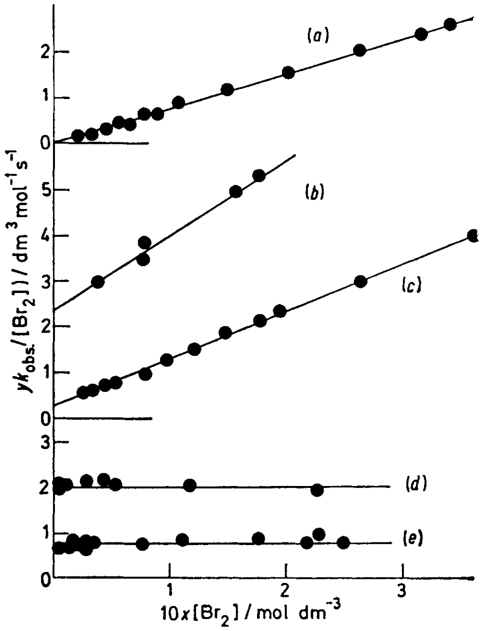

FIGURE 1 $[Br_2]$-dependence of reactions of $[Mn_2(CO)_8L_2]$: (*a*) L = PPh_3, $y = 10^{-2}$, $x = 2$; (*b*) L = $P(OMe)_3$, $y = 10^{-1}$, $x = 4$; (*c*) L = $P(OPh)_3$, $y = 10^{-1}$, $x = 0.4$; (*d*) L = PBu_3, $y = 10^{-3}$, $x = 5$; and (*e*) L = PEt_3, $y = 10^{-3}$, $x = 2$

Values of the activation parameters (Table 3) were estimated by a least-squares analysis weighted according to the uncertainties derived for the values of k_2 and k_3 at each temperature. For L = PPh_3, k_2 was estimated only at 24.6 °C where it was found to be relatively quite small. Values of $\Delta H_3^‡$ and $\Delta S_3^‡$ were calculated from values of k_3 given by $k_{obs.}/[Br_2]^2$.

TABLE 2

Rate constants for the reactions of $[Mn_2(CO)_8L_2]$ with Br_2 in cyclohexane according to the rate equation $k_{obs.} = k_2[Br_2] + k_3[Br_2]^2$ (except where indicated otherwise)

L	θ_c / °C	k_2 / dm^3 mol^{-1} s^{-1}	$10^{-3}k_3$ / dm^6 mol^{-2} s^{-1}	$\sigma(k_{obs.})$ / %
$PEtPh_2$	24.8	192 ± 2	7.32 ± 0.41	2.4
	31.5	258 ± 22	8.35 ± 3.47	10.9
	39.0	361 ± 18	3.62 ± 2.87	6.7
	45.9	424 ± 26	4.43 ± 3.59	8.8
$P(C_6H_{11})_3$ [a]	25.0	18.6 ± 1.4	0.909 ± 0.114	7.8
$P(OMe)_3$	25.1	17.9 ± 1.5	7.85 ± 0.23	10.0
	30.7	19.8 ± 2.3	8.93 ± 0.31	4.9
	37.4	41.8 ± 5.1	8.40 ± 0.69	9.0
	45.8	50.0 ± 10.5	9.25 ± 1.23	13.2
$P(OPh)_3$	25.0	2.28 ± 0.28	0.418 ± 0.014	6.8
	29.5	2.09 ± 1.08	0.506 ± 0.041	12.0
	36.0	1.52 ± 1.01	0.560 ± 0.041	12.3
	44.1	1.21 ± 1.44	0.608 ± 0.050	9.9
PPh_3	24.6	3.62 ± 2.07	14.9 ± 0.7	8.9
	24.6	0 [b]	15.6, 15.2, 15.1	18.0
	32.0 ±0.2	0 [b]	17.3, 15.7, 16.9	
	37.8 ±0.1	0 [b]	21.9, 17.1, 16.5	
	44.9 ±0.1	0 [b]	20.0, 24.1, 19.6	
PPh_3 [c]	24.9	116 ± 6	40 ± 2	9.7
	29.3	281 ± 25	142 ± 11	8.4
	34.9	380 ± 19	120 ± 6	5.5
	39.3	384 ± 28	148 ± 16	8.8
PPh_3 [d]	24.8	0 [b]	17.3 ± 0.06	9.7

[a] $10^3k_1 = 10.3 \pm 2.2$ s^{-1}. [b] Set to zero so that $k_3 = k_{obs.}/[Br_2]^2$. [c] $[MnRe(CO)_8(PPh_3)_2]$. [d] $[Re_2(CO)_9(PPh_3)]$.

When L = $P(C_6H_{11})_3$ the analysis was complicated by the presence of a term in the rate equation that was independent of $[Br_2]$. The data were first analysed graphically according to the equation $k_{obs.} = k_1 + k_2[Br_2] + k_3[Br_2]^2$ in order to obtain approximate values of k_1, k_2, and k_3. These values were then used as initial values in a computer program where the initial values were adjusted to provide a minimum value for $\Sigma[(k_{obs.} - k_{calc.})/k_{calc.}]^2$ by use of the subroutine VA04A.[12]

Reaction of Br_2 *with* $[Mn_2(CO)_9(PPh_3)]$.—This reaction showed the most complicated dependence on $[Br_2]$. The gradients of plots of log $k_{obs.}$ against log$[Br_2]$ decreased from 2.05 ± 0.05 at 25 °C to *ca.* 1 at 42 °C. The best fit of the data at 25.0 °C (22 values of $k_{obs.}$ with $10^3[Br_2] = 1.08$—11.2 mol dm^{-3}) is obtained by a weighted, linear, least-squares analysis according to the equation $k_{obs.}/[Br_2]^2 = k_3 + k_4[Br_2]$ but this equation led to negative values for k_4 at higher temperatures. The best fit at 29.7 °C was obtained from a weighted, non-linear, least-squares analysis (using the VA04A program) according to $k_{obs.}/[Br_2] = k_2 + k_3[Br_2] + k_4[Br_2]^2$ but at 37.1 and 42.0 °C even this led to

TABLE 3

Activation parameters for reactions of $[M_2(CO)_8L_2]$ with Br_2

M	L	$\Delta H_2^‡$ / kJ mol^{-1}	$\Delta S_2^‡$ / J K^{-1} mol^{-1}	$\Delta H_3^‡$ / kJ mol^{-1}	$\Delta S_3^‡$ / J K^{-1} mol^{-1}	$\sigma(k_{obs.})$ / %
Re	PPh_3	23.5 ± 2.7	−80.9 ± 10.0			13.0
Mn	PBu_3	24.1 ± 1.6	−100 ± 6			9.1
Mn	PEt_3	20.7 ± 2.3	−120 ± 9			11.3
Mn	$PEtPh_2$	29.1 ± 1.6	−104 ± 5	−20.8 ± 15.5	−298 ± 52	
Mn	$P(OMe)_3$	42.7 ± 7.5	−78 ± 25	5.4 ± 4.1	−152 ± 13	
Mn	$P(OPh)_3$	−28 ± 24	−334 ± 81	14.1 ± 3.4	−147 ± 11	
Mn	PPh_3			10.1 ± 2.8	−131 ± 9	18.0

negative values for k_4. A reasonably good fit for the data at 37.1 °C was obtained from $k_{obs.}/[Br_2] = k_2 + k_3[Br_2]$ but the data at 42.0 °C were best fitted to $k_{obs.} = a + k_2[Br_2]$. As shown by the results in Table 4, all the values of $\sigma(k_{obs.})$ are quite large but the plots of the data shown in Figure 2 show that the trends are quite clear.

TABLE 4

Rate constants for reaction of $[Mn_2(CO)_9(PPh_3)]$ with Br_2 in cyclohexane according to the rate equation $k_{obs.} = k_2[Br_2] + k_3[Br_2]^2 + k_4[Br_2]^3$

θ_c/°C	k_2/dm^3 mol^{-1} s^{-1}	k_3/dm^6 mol^{-2} s^{-1}	k_4/dm^9 mol^{-3} s^{-1}	$\sigma(k_{obs.})$/%
25.0	0 [a]	33.8 ± 2.7	242 ± 47	21.9
29.7	1.14 ± 0.20	24.6 ± 12.6	213 ± 11	14.9
37.1	1.15 ± 0.16	32.2 ± 3.3	0 [a]	17.8
42.0	4.15 ± 0.24 [b]	0 [a]	0 [a]	18.9

[a] Set to zero. [b] Fitted to $k_{obs.} = a + k_2[Br_2]$, $a = -0.016 \pm 0.002$ s^{-1}.

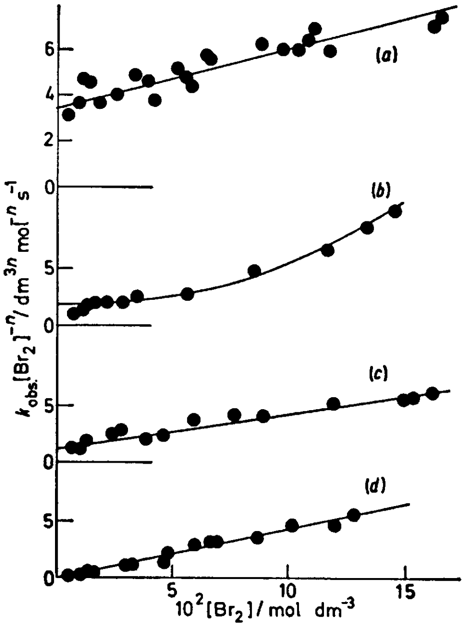

FIGURE 2 $[Br_2]$-dependence of the reaction of $[Mn_2(CO)_9(PPh_3)]$: (*a*) at 25 °C, $n = 2$; (*b*) at 29.7 °C, $n = 1$; (*c*) at 37.1 °C, $n = 1$; and (*d*) at 42.0 °C, $n = 0$

At higher temperatures the reaction was characterized by initial immeasurably rapid changes in the absorbance before the occurrence of the measurably slow reaction but this fast reaction was difficult to quantify and was not investigated further.

DISCUSSION

The occurrence of orders as high as three with respect to $[Br_2]$ and of one case with an immeasurably rapid initial change of absorbance suggests that the reactions proceed *via* the very rapid reversible formation of complex–bromine adducts which then undergo a relatively slow redox process as shown in equations (1)—(3). The rate equation for this mechanism is shown in equation (4). $k_{obs.}$ is the pseudo-first-order rate constant observed at a particular value of $[Br_2]$. In cases where the overall formation constants β_1, β_2, and β_3 are small enough, the denominator in (4) will be indistinguishable from unity and $\beta_1 k_1'$, $\beta_2 k_2'$, and $\beta_3 k_3'$ will be equal, respectively, to the rate constants k_2, k_3, and k_4 obtained from the dependence of $k_{obs.}$ on $[Br_2]$. Even if β_1, *etc.* were to be significant the values of k_2 obtained from the extrapolation of $k_{obs.}/[Br_2]$ to $[Br_2] = 0$ (exemplified in Figure 1) would provide meaningful values of $\beta_1 k_1'$. The only case where a significant rate term independent of $[Br_2]$ is observed is in the reaction of $[Mn_2(CO)_8\{P(C_6H_{11})_3\}_2]$. No rapid initial spectroscopic changes were observed of the sort expected from rapid and complete initial formation of the adduct $[Mn_2(CO)_8\{P(C_6H_{11})_3\}_2(Br_2)]$. The complex is also known to undergo ready thermal homolytic fission [9] and a rate term independent of $[Br_2]$ is not, therefore, unexpected. Although the value of k_1 at 25 °C is *ca.* 10 times greater than that for homolytic fission [9] the possibility of a short-chain reaction initiated by homolytic fission cannot be discounted. Alternatively, this fission process may be initiated by the spectrophotometer light. Photochemically induced reactions of such complexes are well known [13] but they are likely to be unimportant for all but the slowest reactions reported here.

$$\text{complex} + Br_2 \overset{\beta_1}{\rightleftharpoons} \text{complex}\cdot Br_2 \xrightarrow{k_1'} \text{products} \quad (1)$$

$$\text{complex} + 2Br_2 \overset{\beta_2}{\rightleftharpoons} \text{complex}\cdot 2Br_2 \xrightarrow{k_2'} \text{products} + Br_2 \quad (2)$$

$$\text{complex} + 3Br_2 \overset{\beta_3}{\rightleftharpoons} \text{complex}\cdot 3Br_2 \xrightarrow{k_3'} \text{products} + 2Br_2 \quad (3)$$

$$k_{obs.} = \frac{\beta_1 k_1'[Br_2] + \beta_2 k_2'[Br_2]^2 + \beta_3 k_3'[Br_2]^3}{1 + \beta_1[Br_2] + \beta_2[Br_2]^2 + \beta_3[Br_2]^3} \quad (4)$$

Thus, we have studied the reactions of Br_2 with $[Mn_2(CO)_8L_2]$ [$L = P(OPh)_3$ or PEt_3] as a function of the slit width of the monochromator in the stopped-flow apparatus. Slit widths were varied from 0.5 to 5.0 mm whereas those usually used were 0.5—1.0 mm. These complexes cover almost the complete range of reactivity observed in this study and concentrations of Br_2 were such that the paths dependent on $[Br_2]$ and $[Br_2]^2$ [for $L = P(OPh)_3$] were both important. The observed rate constants were independent of slit width. The averages of five measurements showed mean deviations below 1% [$L = P(OPh)_3$] and 2% ($L = PEt_3$) and the contribution of a photochemically initiated pathway to these reactions is quite negligible. We believe, therefore, that the value of k_2 obtained for $[Mn_2(CO)_8\{P(C_6H_{11})_3\}_2]$ can validly be assigned to $\beta_1 k_1'$ and compared with the values of k_2 obtained for the other complexes, and that in general the observed rate constants relate to thermal and not photochemical processes.

The values of k_2 are very dependent on the nature of the metals. For $[M_2(CO)_8(PPh_3)_2]$ k_2 decreases sharply along the series $M_2 = Re_2$, MnRe, and Mn_2. This trend can be correlated quantitatively with the half-wave potentials[14] for the irreversible polarographic reduction of the complexes. $\Delta G^{\ddagger}$ for oxidation by Br_2 increases linearly with $E_{\frac{1}{2}}$ as shown in Figure 3 where values of $E_{\frac{1}{2}}$ are given in the same units as those of $\Delta G^{\ddagger}$. The gradient of the plot is *ca.* 0.4 so that the relation between the ease of chemical oxidation and the difficulty of electrochemical reduction is a close one. This trend is in the opposite direction to that shown by the ease of homolytic fission of the M–M bond in these complexes which is Mn–Mn > Mn–Re > Re–Re.[9] The values of k_2 also confirm that substitution into the decacarbonyls increases the rates of reaction with Br_2. The complex $[Re_2(CO)_{10}]$ reacts slowly[15] in contrast to the rapid reactions of the mono- and bis-(triphenylphosphine) complexes. The value of k_2 for the bis complex is at least 10^5 times that for the mono complex. Substitution of the two axial CO ligands in $[Mn_2(CO)_{10}]$, $[MnRe(CO)_{10}]$, and $[Re_2(CO)_{10}]$ by PPh_3 also brings about an increase in the difficulty of reduction, *i.e.* $E_{\frac{1}{2}}$ becomes more negative in each case.[14]

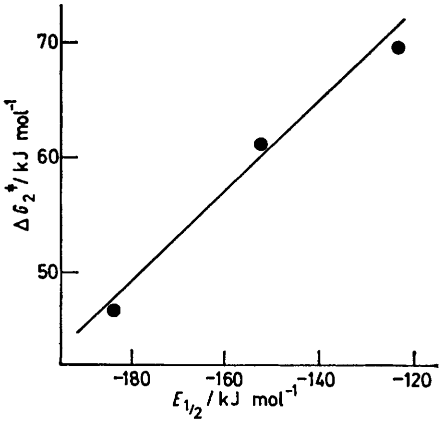

FIGURE 3 Inverse relationship between kinetic ease of oxidation of $[M_2(CO)_8(PPh_3)_2]$ by Br_2 and thermodynamic ease of reduction (M_2 = Mn_2, MnRe, or Re_2)

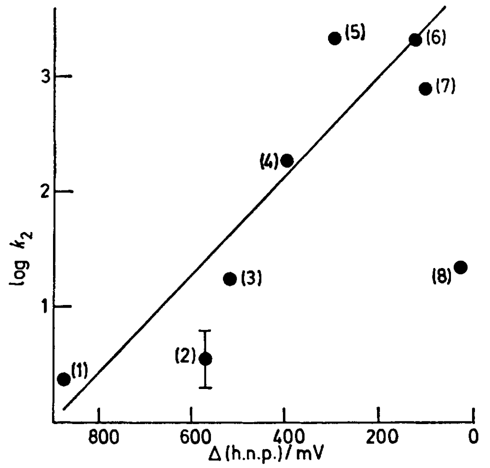

FIGURE 4 Dependence of log k_2 for reaction of $[Mn_2(CO)_8L_2]$ on σ basicity of L. L = $P(OPh)_3$ (1), PPh_3 (2), $P(OMe)_3$ (3), $PEtPh_2$ (4), PEt_2Ph (5), PBu_3 (6), PEt_3 (7) or $P(C_6H_{11})_3$ (8)

The dependence of k_2 on the nature of the substituent in $[Mn_2(CO)_8L_2]$ can be seen from the plot (Figure 4) of log k_2 against the σ basicity of L as measured by the relative half-neutralization potentials, Δ(h.n.p.).[16] Lower values of Δ(h.n.p.) correspond to greater basicity. Although no values of $E_{\frac{1}{2}}$ are available for these complexes it is known that the ease of reduction of the complexes $[Co_2(CO)_6L_2]$ decreases regularly with increasing basicity of L.[17] It seems likely, therefore, that the close inverse correlation between ease of oxidation by Br_2 and ease of electrochemical reduction described above will be maintained in the complexes $[Mn_2(CO)_8L_2]$. Although the linearity of the plot in Figure 4 is not particularly good it does emphasize the deviant behaviour of $[Mn_2(CO)_8\{P(C_6H_{11})_3\}_2]$ for which the low value of k_2 suggests the importance of steric retardation in these reactions. Some steric inhibition may also be operative with $[Mn_2(CO)_8(PPh_3)_2]$. By contrast, the basicity of these substituents has little effect on the rates of homolytic fission of the Mn–Mn bonds which are controlled mainly by steric effects, larger substituents increasing the rates.[9]

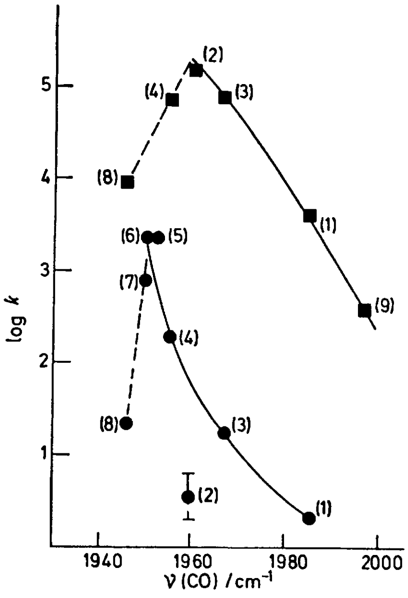

FIGURE 5 Dependence of log k_2 (●) and 1 + log k_3 (■) on ν(CO) for $[Mn_2(CO)_8L_2]$ [L = $P(OPh)_3$ (1), PPh_3 (2), $P(OMe)_3$ (3), $PEtPh_2$ (4), PEt_2Ph (5), PBu_3 (6), PEt_3 (7), or $P(C_6H_{11})_3$ (8)] and $[Mn_2(CO)_9(PPh_3)]$ (9)

Increasing basicity of the substituents generally shows itself in decreasing values of the C–O stretching frequencies and a clear dependence of log k_2 on ν(CO) is apparent from Figure 5 where the deviations due to the PPh_3 and $P(C_6H_{11})_3$ substituents are also obvious. Since lower C–O stretching frequencies are associated with higher electron densities on the CO ligands the results strongly suggest that the reactions involve electrophilic attack by Br_2. Direct attack at the metal atoms is most unlikely because it should be subject to very large steric inhibition. Electrophilic attack at metal atoms in mononuclear carbonyls does appear to occur but only in cases where the metal atom is known to be able to expand its co-ordination number.[18] No such expansion is known for octahedral manganese complexes such as these. Even attack at a C atom, supposing the electron density there were sufficient, would be likely to give rise to steric control of the rate [19] so attack must occur at the O atoms of the carbonyl ligands. The steric effect of $P(C_6H_{11})_3$ substituents is not unexpected. Apart from having a very large cone angle,[20] the ligand is large enough to extend well beyond the end of the equatorial carbonyl groups.[21]

The trends in the values of k_3 (Table 2 and Figure 5) are similar to those of k_2 in so far as comparable values are available. The apparent absence of values of k_3 for $[Mn_2(CO)_8L_2]$ (L = PBu_3, PEt_3, or PEt_2Ph) was thought to be associated with the particularly high values of k_2 for those complexes. An attempt was made to obtain an approximate value of k_3 for $[Mn_2(CO)_8(PEt_2Ph)_2]$ by a least-squares analysis of the data according to the equation $k_{obs.}/[Br_2] = k_2 + k_3[Br_2]$. The plot of $k_{obs.}/[Br_2]$ against $[Br_2]$, however, is curved, values of $k_{obs.}/[Br_2]$ decreasing with $[Br_2]$. A weighted least-squares analysis in terms of the equation $k_{obs.} = (k_2[Br_2] + k_3[Br_2]^2)/(1 + \beta_1[Br_2])$ was performed using the VAO4A program.[12] A much improved fit to the data was obtained as shown in Table 5. The values obtained for k_2, k_3, and β_1 are, however, rather imprecise. The very different values $k_2 = 3.2 \times 10^3$ dm^3 mol^{-1} s^{-1}, $k_3 = 1.45 \times 10^7$ dm^6 mol^{-2} s^{-1}, and $\beta_1 = 10.3 \times 10^3$ dm^3 mol^{-1} correspond to $\sigma(k_{obs.}) = 4.3\%$, *i.e.* the fit is not very much worse. Nevertheless, initial values differing from the best ones by as much as two orders of magnitude still lead to the same final ones so that finite and substantial values for k_3 and β_1 are unambiguously indicated by the kinetic data for the complex. The value of k_2 is not greatly affected by the different analyses. Finite values of k_3 and β_1 are not, however, indicated by the data for L = PBu_3 or PEt_3, any attempt to force finite values leading to pronounced increases in $\sigma(k_{obs.})$. Analysis of the data for L = $PEtPh_2$ according to the equation including β_1 led to negligible values of β_1 and values of k_2 and k_5 essentially unchanged from those in Table 2. Thus, only for L = PEt_2Ph is pre-association of a Br_2 with the complex clearly indicated by the kinetics.

TABLE 5

Kinetic data for the reaction of Br_2 with $[Mn_2(CO)_8(PEt_2Ph)_2]$ in cyclohexane at 25 °C

$10^4[Br_2]$ / mol dm^{-3}	$k_{obs.}$ / s^{-1}	$10^{-3}k_2$ [a] / dm^3 mol^{-1} s^{-1}	$100(k_2 - \bar{k}_2)/\bar{k}_2$ [b] / %	$100(k_{obs.} - k_{calc.})/k_{calc.}$ [c] / %
1.71	0.333	1.94	18.6	−1.33
1.86	0.358	1.92	17.4	−1.64
2.56	0.479	1.87	14.2	−1.28
2.78	0.520	1.87	14.2	−0.47
3.69	0.703	1.91	16.4	4.86
4.64	0.841	1.81	10.6	2.67
5.57	0.969	1.74	6.1	0.94
6.49	1.09	1.68	2.5	−0.44
8.35	1.42	1.70	3.4	4.04
9.23	1.49	1.62	−1.5	0.56
9.79	1.52	1.55	−5.4	−2.57
12.2	1.84	1.50	−8.5	−3.04
12.2	1.87	1.53	−6.4	−0.77
13.9	2.00	1.44	−12.2	−5.41
13.9	2.03	1.46	−11.1	−4.23
19.8	2.93	1.48	−9.5	1.66
19.8	2.95	1.49	−8.9	2.39
27.2	3.82	1.40	−14.4	−0.50
27.6	3.85	1.40	−14.3	−0.85
27.6	4.05	1.47	−10.5	4.12

[a] $k_2 = k_{obs.}/[Br_2]$. [b] $\bar{k}_2$ = average value of $k_2 = (1.64 \pm 0.04) \times 10^3$ dm^3 mol^{-1} s^{-1}; $\sigma(k_2) = \pm 11.8\%$. [c] $k_{calc.} = (k_2[Br_2] + k_3[Br_2]^2)/(1 + \beta_1[Br_2])$ where $k_2 = 2.19 \times 10^3$ dm^3 mol^{-1} s^{-1}, $k_3 = 2.21 \times 10^6$ dm^6 mol^{-2} s^{-1}, $\beta_1 = 1.77 \times 10^3$ dm^3 mol^{-1}, and $\sigma(k_{obs.}) = 3.2\%$.

The occurrence of pre-association and of terms first and second order in $[Br_2]$ is not uncommon in electrophilic reactions of Br_2 with unsaturated hydrocarbons.[22] Terms of higher order than second have also been detected.[22] The path second order in $[Br_2]$ is also accelerated by electron-releasing groups attached to the unsaturated C atoms.[23] The similarity of the effect of substituents on k_2 and k_3 for these reactions suggested that the role of the second Br_2 molecule in the overall third-order path may be to stabilize the dipolar Br(δ−)-Br(δ+) in the transition state by attachment at the negative end.[23] However, the occurrence of a term *third* order in $[Br_2]$ in one of our reactions shows that rapidly formed adducts containing at least two Br_2 molecules can be formed and the role of the Br_2 in the adducts may merely be to act in a rather general inductive way to remove electron density from the metal atoms and weaken the metal–metal bonds until they undergo rapid homolytic fission. The radicals so formed will then react with any Br_2 molecules available and not *necessarily* those originally present in the adduct.

Since some considerable charge separation in the transition states is implied the effect of changing the solvent was investigated for the reaction of $[Mn_2(CO)_8$-

TABLE 6

Solvent effects on the reaction of $[Mn_2(CO)_8\{(POMe)_3\}_2]$ with Br_2 at 25 °C

Solvent	Rate equation for $k_{obs.}$	$\frac{k_2}{dm^3\ mol^{-1}\ s^{-1}}$	$\frac{k_3}{dm^6\ mol^{-2}\ s^{-1}}$	$\frac{\beta_1}{dm^3\ mol^{-1}}$	$\frac{\beta_2}{dm^6\ mol^{-2}}$
C_6H_{12}	$k_2[Br_2] + k_3[Br_2]^2$	17.9	2.85×10^3		
MeOH	$k_3[Br_2]^2/(1 + \beta_1[Br_2] + \beta_2[Br_2]^2)$		4.57×10^7	6.43×10^3	1.24×10^5
CH_2Cl_2	$k_2[Br_2]/(1 + \beta_1[Br_2])$	3.61×10^4		44.7	
CCl_4	$k_2[Br_2]/(1 + \beta_1[Br_2])$	3.85×10^3		34.0	

$\{P(OMe)_3\}_2]$, with the results shown in Table 6. $[Br_2]$ was varied over the range *ca.* 10^{-4}—10^{-2} mol dm^{-3} and a very pronounced dependence on solvent was observed. Reaction in MeOH was very much faster, and kinetic evidence for the rapid formation of the adducts $[Mn_2(CO)_8\{P(OMe)_3\}_2(Br_2)]$ and $[Mn_2(CO)_8\{P(OMe)_3\}_2(Br_2)_2]$ was provided by the form of the rate equation. The non-detection of a term first order in $[Br_2]$ shows that $k_2 \lesssim 10^3$ dm^3 mol^{-1} s^{-1} so that $k_1' = k_2/\beta_1 \lesssim 10^{-1}$ as compared to $k_2' = k_3/\beta_2 =$ *ca.* 400. The more polar solvent therefore increases the values of k_3 and, probably, of k_2, and it enhances the formation of adducts containing one or two molecules of Br_2. The adduct containing two molecules of Br_2 is over 10^3 times more reactive than that containing only one. The effect of CH_2Cl_2 and CCl_4 as solvents is also to accelerate the overall reaction and enhance the formation of adducts. However, the rate equation gives evidence for the formation of an adduct only with one Br_2 molecule and reaction *via* the 1 : 2 (Br_2) adduct seems to be unimportant. The formation constant of the 1 : 1 (Br_2) adduct is also very much less favoured than in MeOH but its reactivity (as defined by k_1') is considerably greater.

These results cannot easily be related to the usual electrical properties of the solvent. For instance, the dielectric constants are in the order C_6H_{12} (2.023), CCl_4 (2.238), CH_2Cl_2 (8.89), and MeOH (32.63) which is not the same as the order of k_2: C_6H_{12}, MeOH $<$ CCl_4 $<$ CH_2Cl_2. Although the dielectric constants of C_6H_{12} and CCl_4 are almost identical, k_2 in the latter is *ca.* 200 times larger. Part of the difficulty may be associated with conflicting effects on β_1 and k_1' (as is shown above to occur) and much more extensive data will have to be accumulated before the effects can be resolved.

The activation parameters shown in Table 3 seem perfectly reasonable for fast redox processes such as these although there are no precisely comparable data. The two negative values for $\Delta H^\ddagger$ are both for relatively quite unimportant reaction paths and are so imprecise that small positive values are not at all improbable. However, for $[Mn_2(CO)_8(PEt_2Ph)_2]$ and $[MnRe(CO)_8(PPh_3)_2]$ the Eyring plots are curves as is not uncommon for reactions involving pre-association and/or several species in the transition state.[24] Negative values of $\Delta H^\ddagger$ would also be quite possible if adduct formation were sufficiently exothermic. The change in rate equation with temperature for the reaction of $[Mn_2(CO)_9(PPh_3)]$ is consistent with the generally lower values of $\Delta H^\ddagger$ for higher-order reactions.

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