Journal of Organometallic Chemistry, 220 (1981) 75—85
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

KINETICS OF HALOGENATION OF $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$

SULTAN AMER, GARY KRAMER and ANTHONY POË *

J. Tuzo Wilson Laboratories, Erindale College, University of Toronto, Mississauga, Ontario L5L 1C6 (Canada)

(Received March 16th, 1981)

Summary

The kinetics of reactions of $Cp_2Mo_2(CO)_6$ ($Cp = \eta^5\text{-}C_5H_5$) with I_2, ICl, Br_2, $CHBr_3$, and $C_2H_2Cl_4$ to form mononuclear halogeno complexes have been studied. Reactions with halogens proceed rapidly at 25°C and the kinetics suggest the involvement of intermediate adducts containing one or two molecules of halogen. Reactions with I_2 and ICl show paths involving transition states that contain two molecules of complex and at least one molecule of halogen. A substantial proportion of the complex appears to form such aggregates in the reaction with ICl. It is suggested that the halogen molecules in the adducts are attached to the O atoms around the periphery of the complex. The results are discussed in the light of mechanisms proposed previously by others. Reactions with $CHBr_3$ and $C_2H_2Cl_4$ proceed cleanly to form $CpMo(CO)_3X$ at 72°C in decalin and a reaction path involving direct attack by two molecules of halocarbon competes with homolytic fission as the rate-determining step.

Introduction

The complex $Cp_2Mo_2(CO)_6$ ($Cp = \eta^5\text{-}C_5H_5$) contains a well defined, single Mo—Mo bond unsupported by bridging carbonyl groups [1]. It undergoes a wide variety of reactions that proceed at greatly different rates. Thus, reaction with iodine proceeds very rapidly in various solvents at room temperature [2,3] to form $CpMo(CO)_3I$ while the complex can be recovered without change after refluxing in toluene for several hours [4]. Decomposition in decalin under atmospheres of oxygen and reactions with $C_{16}H_{33}I$ to form $CpMo(CO)_3I$ proceed measurably slowly even at 135°C [5]. Homolytic fission of the Mo—Mo bond has been assigned as the rate-determining step of these reactions and the activation enthalpy was found to be 135.9 ± 2.2 kJ mol^{-1}. The rapid and very clean reaction with I_2 must therefore be going via some mechanism other than rate-determining homolytic fission. We report here a study of the kinetics of

0022-328X/81/0000—0000/$02.50

that reaction and of reactions with iodine monochloride, bromine, bromoform, and 1,1,2,2-tetrachloroethane.

Experimental

The complex $Cp_2Mo_2(CO)_6$ (Strem Chemicals, Inc.) was used as received as were $CHBr_3$ (BDH Chemicals) and *syn*-$C_2H_2Cl_4$ (Fischer; Scientific Grade). All other reagents were obtained and treated as described elsewhere and the general procedures for following the reactions and analysing the data have also been fully described [6,7]. Dilute solutions of $Cp_2Mo_2(CO)_6$ are very sensitive to exposure to laboratory light and solutions were made up in red light freshly for each run or closely related sets of runs. No attempt was made to exclude oxygen since the complex is quite insensitive to O_2 in the dark [5].

Results

Reactions of $Cp_2Mo_2(CO)_6$ with I_2, Br_2 and ICl

Reactions were followed by monitoring the decreasing absorbance of the complex at 390 nm (ϵ 2.0×10^4 dm^3 mol^{-1} cm^{-1} in cyclohexane) by means of a "Canterbury" stopped-flow spectrophotometer [6] or Cary 16K spectrophotometer operating on the continuous drive mode. Decreases of a factor of 5—10 in the absorbance were typical.

Reaction with I_2 in cyclohexane led to $CpMo(CO)_3I$ as the only observable product as evidenced by the IR spectrum [3] after complete loss of $Cp_2Mo_2(CO)_6$ (ν(CO) 2045s, 1975s, and 1960s cm^{-1}). Half times of reaction varied from ca. 1 min to 20 h. Slower reactions showed no dependence on whether the sample was kept in the spectrophotometer light beam during the whole period of reaction or removed between measurements. Reproducibility of runs within closely related sets was excellent while reproducibility between sets of runs was not so good, possibly because of partial and variable decomposition on making up solutions. The form of the dependence on concentrations was, however, quite consistent from one set of runs to another, e.g. eq. 1 below. Initial gradients of the rate plots were used to estimate initial rates, R_0. These were found to depend on C_0, the initial concentration of $Cp_2Mo_2(CO)_6$, according to eq. 1. Both k_a and k_b were dependent on $[I_2]$.

$$R_0 = k_a C_0 + k_b C_0^2 \tag{1}$$

The dependence of $k_{obs}/[I_2] = R_0/C_0[I_2]$ on $[I_2]$ at $C_0 = 1 \times 10^{-5}$ mol dm^{-3} is shown in Fig. 1. The line drawn through the points was calculated according to eq. 2 and the parameter values given in Table 1 *. k_3 can be

$$k_{obs} = R_0/C_0 = k_3[I_2]^2/\{1 + \beta_1[I_2] + \beta_2[I_2]^2\} \tag{2}$$

obtained from values of k_{obs} at low concentrations of I_2. The need to include the term containing β_2 is clearly apparent from the significant gradient of a plot of $\{k_3[I_2]^2 - k_{obs}\}/k_{obs}[I_2]$ against $[I_2]$, the value of the former increasing by a

---

* Tables of supplementary data are avilable from the authors on request.

TABLE 1

KINETIC PARAMETERS FOR REACTIONS OF HALOGENS WITH $Cp_2Mo_2(CO)_6$ AT 25°C

X_2	10^3 [X_2], (mol dm^3)	10^5 C_0 (mol dm^3)	No. of runs	Rate eq. [a]	Values of parameters	$\sigma(k_{obs})$, [b] (%)
I_2 [c]	2.67	2.49–18.5	8	1	$k_a = (3.7 \pm 1.0) \times 10^{-4}$ s^{-1} $k_b = (7.7 \pm 1.5)$ dm^3 mol^{-1} s^{-1}	12
	10.9	1.0–10.0	10	1	$k_a = (5.1 \pm 0.8) \times 10^{-3}$ s^{-1} $k_b = (80.5 \pm 16)$ dm^3 mol^{-1} s^{-1}	16
	0.291–18.5	1.0	14	2	$k_3 = 110$ dm^6 mol^{-2} s^{-1} $\beta_1 = 40$ dm^3 mol^{-1} $\beta_2 = 6 \times 10^3$ dm^6 mol^{-2}	5.5
ICl [c]	0.519	0.354–2.48	9	3	$k_b = (1.9 \pm 0.1) \times 10^5$ dm^3 mol^{-1} s^{-1} $K = (2.1 \pm 0.1) \times 10^5$ dm^3 mol^{-1}	3.4
	0.206–3.30	1.53	10	4	$k_2 = 113 \pm 51$ dm^3 mol^{-1} s^{-1} $k_3 = (2.1 \pm 0.1) \times 10^6$ dm^6 mol^{-2} s^{-1}	8.0
Br_2 [d]	1.39	0.42–1.7	5	—	$k_3 = (1.70 \pm 0.14) \times 10^5$ dm^6 mol^{-2} s^{-1}	15.0
	0.42–1.98	1.7	11	—	$k_3 = (1.76 \pm 0.02) \times 10^5$ dm^6 mol^{-2} s^{-1}	5.2

[a] See text. [b] Standard deviation for measurement of an individual rate constant. [c] In cyclohexane. [d] In t-Bu_2O.

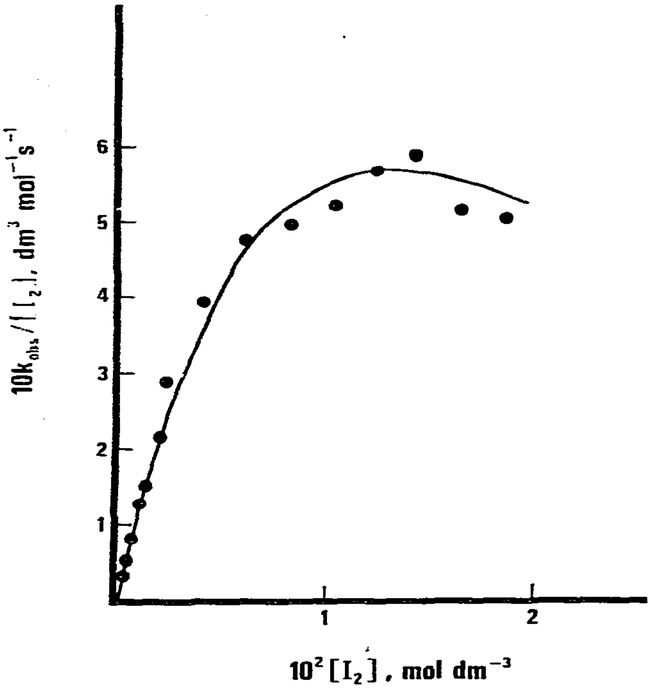

Fig. 1. Dependence of k_{obs} on $[I_2]$ for reaction of $Cp_2Mo_2(CO)_6$ with I_2 at 25°C and with $[Cp_2Mo_2(CO)_6] = 1 \times 10^{-5}$ mol dm^{-3}. The continuous line through the data is drawn according to eq. 2 with $k_3 = 110$ dm^6 mol^{-2} s^{-1}, $\beta_1 = 40$ dm^3 mol^{-1}, and $\beta_2 = 6 \times 10^3$ dm^6 mol^{-2}. The standard deviation, $\sigma(k_{obs})$, of the data from the line is 5.5%.

factor of ca. 3 over the range of $[I_2]$ used instead of remaining constant as would have been the case if β_2 were negligible. Under these conditions most of the reaction is going via the path first order in C_0. The dependence of k_{obs} on $[I_2]$ at high values of C_0 was pronounced but the data were not so reproducible as those at lower C_0 and no quantitative analysis was possible.

Reaction with ICl in cyclohexane occurred in two quite distinct steps. The first involved loss of IR bands due to $Cp_2Mo_2(CO)_6$ and formation of a number of other bands including ones at 1903 and 1913 cm^{-1} in addition to ones assignable to $CpMo(CO)_3I$. These were all replaced during the second stage by bands at 2090 and 2058 cm^{-1} and formation of a yellow precipitate. The first stage was followed by monitoring the very substantial loss of absorbance at 390 nm. Half lives varied from ca. 20 ms to 7 s. Initial gradients of pseudo first order rate plots were used to obtain values of R_0 which gave an excellent fit to eq. 3 as shown by a good linear plot of

$$R_0 = k_b C_0^2 / \{1 + KC_0\} \tag{3}$$

C_0/R_0 against $1/C_0$ and by the plot shown in Fig. 2.

The dependence of k_{obs} on [ICl] gave an excellent fit to eq. 4 as shown

$$k_{obs} = R_0/C_0 = k_2[\mathrm{ICl}] + k_3[\mathrm{ICl}]^2 \tag{4}$$

in Fig. 3. k_2 is relatively quite small and not well defined.

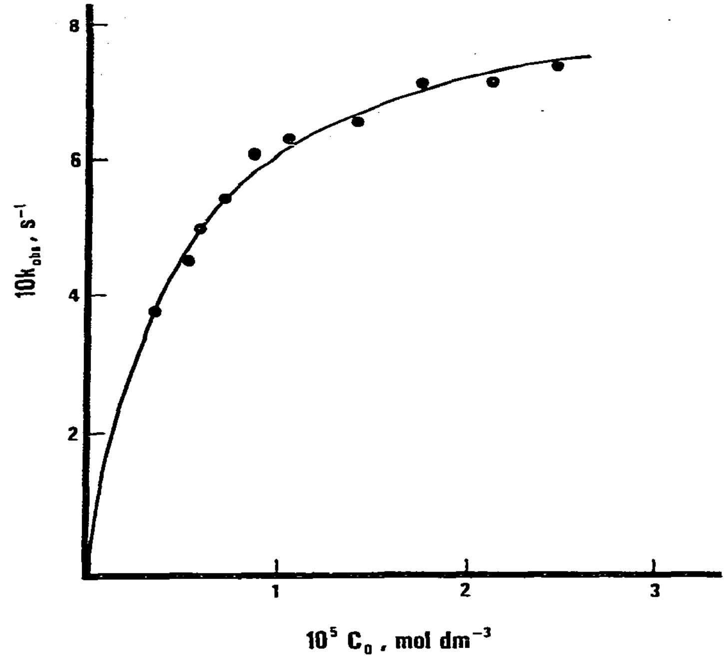

Fig. 2. Dependence of k_{obs} on C_0 at 25°C and with [ICl] = 5.19×10^{-4} mol dm^{-3}. The continuous line is calculated according to eq. 3 with $k_{obs} = R_0/C_0$, $k_b = 1.91 \times 10^5$ dm^3 mol^{-1} s^{-1}, and $K = 2.14 \times 10^5$ dm^3 mol^{-1}. $\sigma(k_{obs}) = 2.8\%$.

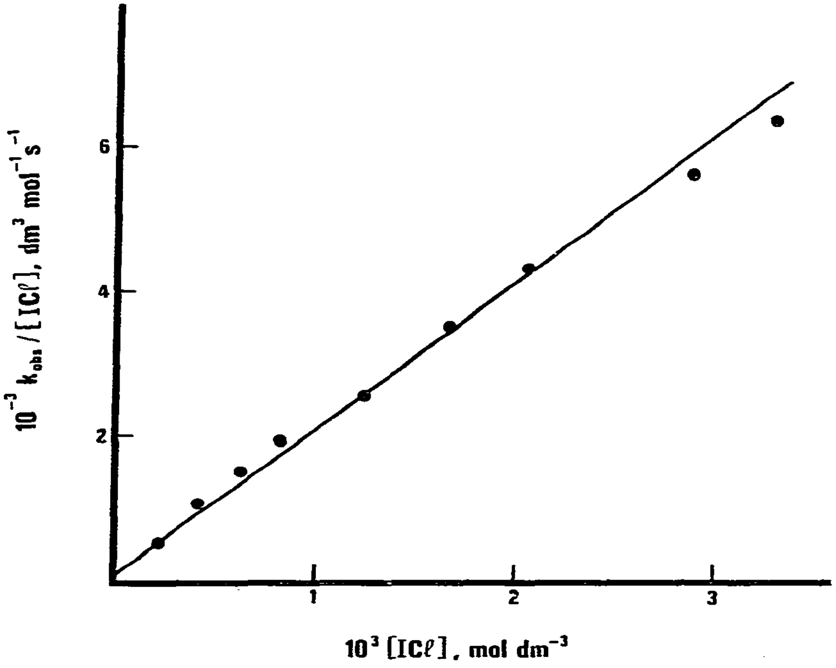

Fig. 3. Dependence of k_{obs} on [ICl] at 25°C and with $C_0 = 1.53 \times 10^{-5}$ mol dm^{-3}. The line is drawn according to eq. 4 with $k_2 = 113$ dm^3 mol^{-1} s^{-1} and $k_3 = 2.1 \times 10^6$ dm^6 mol^{-2} s^{-1} and $\sigma(k_{obs}) = 6.6\%$.

Reaction with Br_2 in cyclohexane led to complete loss of spectral bands due to $Cp_2Mo_2(CO)_6$ but was complicated by formation of a pale orange precipitate. Reaction in ditertiarybutyl ether was not accompanied by precipitation and the kinetics were followed in this solvent. No clear bands due to formation of any carbonyl-containing product could be observed, however. Excellent pseudo first-order rate plots were obtained by following the decreasing absorbance at 390 nm and the rate constants were independent of C_0 over the range (4.2—17) × 10^{-6} mol dm^{-3} when $[Br_2] = 1.39 \times 10^{-3}$ mol dm^{-3}. The dependence of k_{obs} on $[Br_2]$ was closely second order over the range (3.74—20.3) × 10^{-4} mol dm^{-3}. Half times of reaction were in the range 0.8—25 s. The kinetic parameters for all these reactions are summarized in Table 1.

Reactions with $C_2H_2Cl_4$ and $CHBr_3$

Reaction with $C_2H_2Cl_4$ in decalin at 72.5°C led cleanly to $CpMo(CO)_3Cl$ (ν(CO) 2070s, 1975(br) cm^{-1}) [3,8,9]. Quite good pseudo first-order rate plots were obtained from the decreasing absorbance at 390 nm but a detailed study of the dependence on C_0 was not undertaken. The dependence of k_{obs} on $[C_2H_2Cl_4]$ is shown in Fig. 4. A small intercept at $[C_2H_2Cl_4] = 0$ is not determined by the data but is assumed because it corresponds to the rate obtained

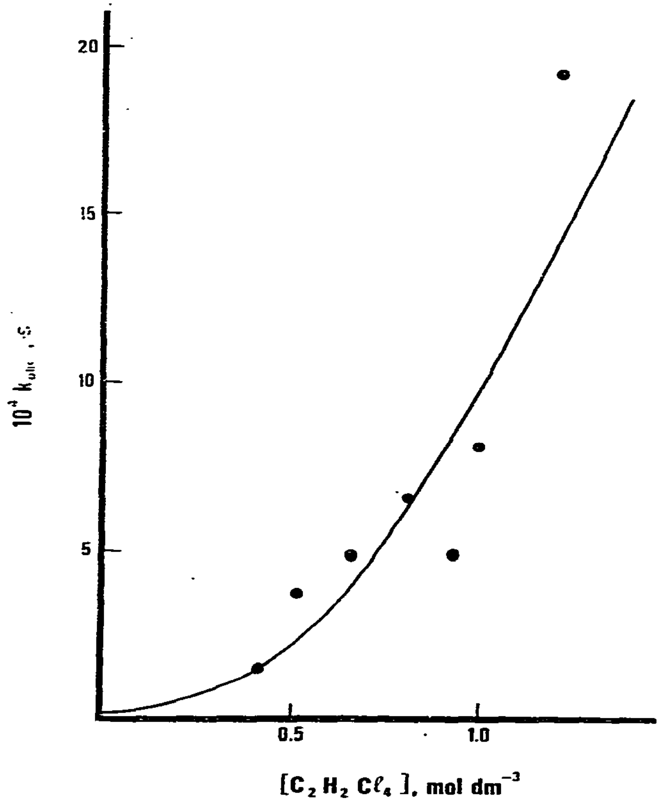

Fig. 4. Dependence of k_{obs} on $[C_2H_2Cl_4]$ at 72.5°C with $C_0 = 2.2 \times 10^{-5}$ mol dm^{-3}. The line is drawn according to $10^4\ k_{obs} = 0.2 + 9.5[C_2H_2Cl_4]^2$ and $\sigma(k_{obs}) \sim 20\%$.

for homolytic fission of $Cp_2Mo_2(CO)_6$ [4]. $C_2H_2Cl_4$ would be expected to scavenge $CpMo(CO)_3^{\cdot}$ radicals very effectively [9]. The increase in k_{obs} with increasing $[C_2H_2Cl_4]$ is very approximately second order in $[C_2H_2Cl_4]$ with a third order rate constant of $(9.5 \pm 1.0) \times 10^{-4}$ dm^6 mol^{-2} s^{-1}.

Reaction with $CHBr_3$ in decalin at 72.2°C led cleanly to $CpMo(CO)_3Br$ (ν(CO) 2050m, 1977s, and 1958s cm^{-1}) [3,8]. The dependence of k_{obs} on $[CHBr_3]$ was also consistent with a second order dependence on the concentration of halogen compound in addition to a path controlled by rate-determining homolytic fission. The third order rate constant is not well defined because the contribution of the homolytic fission path to the rate is relatively much greater than in the reaction with $C_2H_2Cl_4$ but its value is ca. 1×10^{-4} dm^6 mol^{-2} s^{-1}.

Discussion

Thorough and very careful preparative studies have been made [3,10] of the reactions of halogens with $Cp_2Mo_2(CO)_6$. A variety of products was observed depending on the particular halogen, the solvent, and other conditions. Reaction with I_2 in ethanol or dichloromethane first forms the iodide-bridged species $\{CpMo(CO)_3\}_2$ $(\mu\text{-I})^+$. This subsequently reacts quite rapidly to form $CpMo(CO)_3I$ which then reacts much more slowly with a sufficient excess of I_2 to form $CpMo(CO)_2I_3$. Reaction with Br_2 in dichloromethane leads rapidly to $CpMo(CO)_3Br$ and then to the rather insoluble orange $CpMo(CO)_2Br_3$. No intermediate Br^--bridged complex was detectable. Reaction with Cl_2 is even faster and only the quite insoluble $CpMo(CO)_2Cl_3$ is formed, even $CpMo(CO)_3Cl$ not being observed as an intermediate. $CpMo(CO)_2Br_3$ and $CpMo(CO)_2Cl_3$ both decompose readily with evolution of CO.

Our reactions are fully consistent with this preparative work. Reaction with a large excess of I_2 in cyclohexane at 25°C formed $CpMo(CO)_3I$ in essentially quantitative yield. Reaction with Br_2 in cyclohexane led to an insoluble orange precipitate, presumably of $CpMo(CO)_2Br_3$, but reaction in t-Bu_2O led to complete reaction without formation of any carbonyl-containing product. $CpMo(CO)_2Br_3$ is quite unstable towards acetone [10] and, evidently, also towards t-Bu_2O. Reaction with ICl in cyclohexane led initially to a species that has not been characterized but the final yellow product is quite insoluble and has bands close to those for $CpMo(CO)_2Cl_3$ [3,10]. The difference is accountable for by solvent effects [11] or even perhaps by formation of a mixed product such as $CpMo(CO)_2ICl_2$. In all the reactions the absorbance at 390 nm, characteristic of the Mo—Mo bond, completely disappeared. There is no doubt, in the light of the preparative work [3,10] and our own results, that all the reactions with halogens that we have been following involve breaking of the Mo—Mo bond and eventual formation of mononuclear carbonyl halides of molybdenum. Whether halide-bridged complexes are formed initially as very reactive intermediates is not evident from our work but seems likely in view of the preparative studies [3]. Although the formation of such intermediates is indicative of the intimate mechanism of the reactions [3] it is not relevant to the stoichiometric mechanism (i.e. the composition of the various transition states) which will be the major subject of the following discussion.

The kinetics all show a more-or-less complex dependence of the rates on the concentration of halogen, terms in [halogen]^2 being observed in all cases. Reaction with I_2 is complicated by the existence of separate terms showing first and second order dependence of the rate on $[Cp_2Mo_2(CO)_6]$. The I_2-dependence was determined at low values of $[Cp_2Mo_2(CO)_6]$ such that most of the reaction (ca. 85%) was occurring via the path that showed a first order dependence on $[Cp_2Mo_2(CO)_6]$. Although the existence of some reaction via the path that was second order in $[Cp_2Mo_2(CO)_6]$ means that the $[I_2]$-dependence is not strictly applicable only to the first-order path, the good fit of the data to eq. 2 as shown in Fig. 1 suggests that any complications arising from the second order path were quite small and did not by themselves lead to the complexity shown by eq. 2. In general, therefore, the kinetics follow the pattern observed for reactions of Br_2 and I_2 with complexes such as $M_2(CO)_{10-n}L_n$ (M = Mn, Re; L = P-donor ligand; n = 1 or 2) [6,7] and of Br_2, I_2, and ICl with $Ru_3(CO)_9(PPh_3)_3$ [12]. These reactions were all concluded to proceed by way of rapid pre-association of the complexes with one or more molecules of halogen, followed by slow unimolecular oxidation and metal—metal bond fission within the adduct, as shown in reactions 5 and 6. Spectroscopic evidence for the formation of

$$\text{Complex} + nX_2 \overset{\beta n}{\rightleftharpoons} \text{Complex}(X_2)_n \tag{5}$$

$$\text{Complex}(X_2)_n \xrightarrow{k_n} \text{products} \tag{6}$$

adducts was observed in some cases [6,12].

It seems entirely reasonable to conclude that the same type of reaction sequence is being followed in the reactions described here. There is, however, a distinctive feature shown by the reactions of $Cp_2Mo_2(CO)_6$ with I_2 and ICl, namely the occurrence of a more complex dependence of the rates on $[Cp_2Mo_2(CO)_6]$. In the case of reaction with I_2 there is the term second order in [complex] in addition to the usual first order one. Since the second order term also shows a dependence on $[I_2]$ we conclude that there is a path contributing to the reaction of the form shown in reactions 7—9. The value

$$\text{Complex} + nI_2 \rightleftharpoons \text{Complex}(I_2)_n \tag{7}$$

$$\text{Complex}(I_2)_n + \text{Complex} \rightleftharpoons \text{Complex}_2(I_2)_n \tag{8}$$

$$\text{Complex}_2(I_2)_n \rightarrow \text{product} \tag{9}$$

of n is not defined by the kinetics but it must be at least 1 because of the qualitative dependence of k_b in eq. 1 on $[I_2]$.

The rate of reaction with ICl depends directly on C_0^2 but also inversely on $(1 + KC_0)$ so that the rate changes smoothly from being second order in [complex] at low C_0 to first order at high C_0. This suggests that an equilibrium equivalent to reaction 8 must be involved and that it lies substantially to the right at higher values of C_0. Reaction appears to occur only when the transition state contains two molecules of complex. The rates also showed first and second order dependence on [ICl], which suggests that the adducts containing 2 molecules of $Cp_2Mo_2(CO)_6$ must contain either 1 or 2 molecules of ICl as well. The equilibrium constant for formation of the adducts containing two molecules of $Cp_2Mo_2(CO)_6$ is such that the rates would simply have been first order in [complex] if the kinetics had been studied with $C_0 \gtrsim 5 \times 10^{-5}$ mol dm^{-3}.

This implies that all the complex would have been present in the form of aggregates containing two molecules of $Cp_2Mo_2(CO)_6$ and one or two molecules of ICl under these conditions. The existence of transition states containing two molecules of metal carbonyl in similar reactions has been indicated before, but not so clearly [6,12].

The reaction of $Cp_2Mo_2(CO)_6$ with I_2 is several orders of magnitude faster than those of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, but considerably slower than the reactions of P-donor-substituted derivatives of those carbonyls [6,7]. The effect of the substituents was concluded to be due to the enhanced transfer of electron density to the metal atoms and thence to the carbonyl ligands. This facilitated the formation of adducts with halogen molecules, as in reaction 7, and facilitated the oxidation of the metal centres. The absence of steric effects with other than the very largest substituent $P(C_6H_{11})_3$ led to the conclusion that the adducts involved attachment of the halogens at the O atoms on the periphery of the complexes so that electron transfer took place through the CO ligands. Direct attack at the metal atom was believed to be virtually impossible for steric reasons and electrophilic attack at the carbon atoms was thought to be unlikely, also for steric reasons.

We believe that a similar situation obtains in the reactions of $Cp_2Mo_2(CO)_6^+$. The increased rates compared with those of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ cannot simply be associated with the lower values of $\nu(CO)$ in $Cp_2Mo_2(CO)_6$. Although this implies a greater electron density on the O atoms and a more ready formation of adducts (as is, in fact, clearly observed with I_2), the subsequent reaction of the adduct will depend on the ease of oxidation of the particular metal atoms in the adduct.

There is, of course, a major difference between the complex studied here and those studied previously [6,7] and that is the presence of the cyclopentadienide ligands. Kobayashi et al. [13] have concluded that tetracyanoethylene forms charge transfer complexes with $AreneCr(CO)_3$ complexes by attachment at the metal. More extensive studies by Sennikov et al. [14] were claimed to show that attachment occurred at the arene ring. The proposition that the halogen molecules form adducts with $Cp_2Mo_2(CO)_6$ by attachment at the far side of the Cp^- ligands from the Mo atoms has, therefore, to be considered. The halogens in such adducts could conceivably withdraw electron density from the Mo—Mo bonding region of the complex and facilitate the breaking of that bond. A process of this sort would be most unlikely to be influenced by steric effects when large substituents replace one or more CO ligands. There is, however, some evidence that steric effects do occur. Thus $Cp_2Mo_2(CO)_4\{P(OPh)_3\}_2$ reacts with I_2 to form $CpMo(CO)_2\{P(OPh)_3\}I$ in benzene only at refluxing temperature and then only over a period of hours [15]. Electronically the introduction of P-donor substituents would be expected greatly to facilitate the reaction [6,7] since such substitution reduces the C—O stretching frequencies substantially [15]. Reaction of I_2 with $Cp_2Mo_2(CO)_4\{P(OMe)_3\}_2$ in ethanol is quite rapid [3] but it is not known whether the greater rate expected (compared with reaction of $Cp_2Mo_2(CO)_6$) because of the electronic effect of P-donor ligands is offset by their size. These $P(OMe)_3$ substituents are larger than CO but substantially smaller than $P(OPh)_3$ [16]. We believe that it is likely, therefore, that the halogen molecules in their reactions with $Cp_2Mo_2(CO)_6$ are attached at or near the O atoms of the CO ligands.

It is interesting to note parenthetically that the electronic effect of substituents is not limited simply to P-donor ligands. Thus, the Me_3Si ligands in $[Me_3SiRu(CO)_4]_2$ are more electron-donating than the Cl_3Si ligands in $[Cl_3SiRu(CO)_4]_2$ as evidenced by the respective C—O stretching frequencies, 2014 and 2056 cm^{-1} [17]. Reaction of the former complex with I_2 in hexane is rapid at 0°C whereas the latter reacts slowly even in refluxing hexane.

As with the corresponding reactions of the complexes $Mn_2(CO)_8L_2$ and $Re_2(CO)_8L_2$, the reaction of Br_2 with $Cp_2Mo_2(CO)_6$ is much faster than that of I_2, as would be expected from its greater electrophilic character. (The effect of the different solvent is likely to be very small [7].) Two molecules of halogen are required in this reaction as in the reaction with I_2. The reaction with ICl is not really comparable since it proceeds through a transition state containing two molecules of complex whereas most of the data for reactions with I_2 and Br_2 were obtained under conditions such that only one molecule of complex was involved in the transition state.

The intimate mechanism of the reactions within the various adducts is not evident from the kinetic data. Haines et al. made the important discovery that the reaction with I_2 proceeds with formation of an intermediate bridged dinuclear cation $Cp(OC)_3Mo{-}I{-}Mo(CO)_3Cp^+$ [3]. It was proposed that this was preceded either by attack at the Mo—Mo bond by one end of an I_2 molecule or by electron transfer within a $Cp_2Mo_2(CO)_6 \cdot I_2$ adduct to form $Cp_2Mo_2(CO)_6^+ \cdot I_2^-$. Since the formation of the bridged cation does not seem to be dependent on the nature of the different solvents used, we believe that these proposals unduly simplify the situation. Our kinetic data show that, under the conditions used in the preparative studies, the transition states involve two molecules of complex and one or more molecules of I_2. Under conditions where reactions proceed through transition states containing only one molecule of complex the transition states also have to contain at least two molecules of halogen. This need for more than just one molecule of halogen is widespread in the reactions of halogens (mainly I_2 and Br_2) with other complexes [6,7,12]. It was suggested [7] that the role of the additional halogen molecules might simply be the additional inductive weakening of the metal—metal bonds by extra withdrawal, through the CO ligands, of electron density from the metal—metal bond region.

The reason why some reactions are greatly facilitated by having two molecules of complex in the transition state is not at all clear. All these transition states contain at least one molecule of halogen and it seems likely that these are sandwiched between the two carbonyl molecules. Otherwise it is difficult to see what would attract two molecules of complex to each other.

Although the kinetic data are not extensive, the reactions with $CHBr_3$ and $C_2H_2Cl_4$ to form $CpMo(CO)_3Br$ and $CpMo(CO)_3Cl$ are of interest. No comparable data for thermal reactions of halocarbons with dinuclear metal carbonyls appear to exist but reactions with mononuclear carbonyls have recently been reviewed [18]. $Mo(CO)_6$ does not react directly with CCl_4 but the much more easily oxidized *cis*-$Mo(CO)_2(dmpe)_2$ reacts with a second order rate constant of 2×10^{-2} dm^3 mol^{-1} s^{-1} at 20°C and with formation of $Mo(CO)_2(dmpe)_2^+$ [19]. In our reactions two molecules of halocarbon appear to be involved in direct attack and this path competes quite successfully with initial homolytic fission [5] as a rate-determining step.

Acknowledgements

We thank Erindale College and the Natural Sciences and Engineering Research Council of Canada for support.

References

1 F.C. Wilson and D.P. Shoemaker, J. Chem. Phys., 27 (1957) 809; Inorg. Chem., 13 (1974) 1086.
2 E.W. Abel, A. Singh and G. Wilkinson, J. Chem. Soc., (1960) 1321.
3 J.C.T.R. Burkett-St. Laurent, J.S. Field, R.J. Haines and M. McMahon, J. Organometal. Chem., 181 (1979) 117.
4 R.J. Klingler, W. Butler and M.D. Curtis, J. Amer. Chem. Soc., 97 (1975) 3535.
5 S. Amer, G. Kramer and A.J. Poë, J. Organometal. Chem., 209 (1981) C28.
6 G. Kramer, J. Patterson and A.J. Poë, J. Chem. Soc. Dalton, (1979) 1167.
7 G. Kramer, J. Patterson, A.J. Poë, and L. Ng, Inorg. Chem., 19 (1980) 1161.
8 T.E. Sloan and A. Wojcicki, Inorg. Chem., 7 (1968) 1268.
9 M.S. Wrighton and D.S. Ginley, J. Amer. Chem. Soc., 97 (1975) 4246.
10 R.J. Haines, R.S. Nyholm and M.H.B. Stiddard, J. Chem. Soc. A, (1966) 1606.
11 P.S. Braterman, Structure and Bonding, 26 (1976) 2.
12 G. Kramer, A.J. Poë and S. Amer, Inorg. Chem., 20 (1981) 1362.
13 H. Kobayashi, M. Kobayashi and Y. Kaizu, Bull. Chem. Soc. Japan, 46 (1973) 3109, 48 (1975) 1222.
14 P.G. Sennikov, V.A. Kuznetsov, A.N. Egorochkin, N.I. Sirotkin, N.G. Nazarova and G.A. Razuvaev, J. Organometal. Chem., 190 (1980) 167.
15 R.J. Haines, R.S. Nyholm and M.H.B. Stiddard, J. Chem. Soc., A (1968) 43.
16 C.A. Tolman, Chem. Rev., 77 (1977) 313.
17 M.J. Ash, A. Brookes, S.A.R. Knox and F.G.A. Stone, J. Chem. Soc. A, (1971) 458.
18 J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978, pp. 194—197.
19 J.A. Connor and P.I. Riley, J. Chem. Soc., Chem. Commun., (1976) 634.