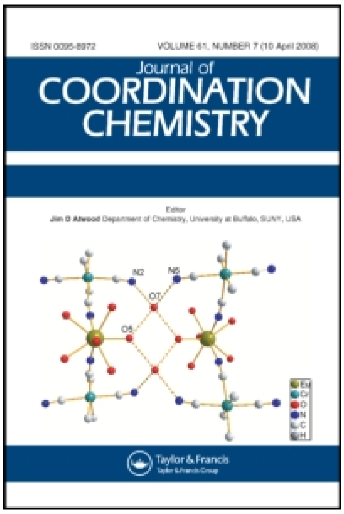

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Octahedral Metal Carbonyls. 68. Kinetics and Mechanism of the Displacement of Chlorobenzene by Piperidine from the Photoproduced [Chlorobenzene-Pentacarbonylchromium(0)] Solvate

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OCTAHEDRAL METAL CARBONYLS. 68. KINETICS AND MECHANISM OF THE DISPLACEMENT OF CHLOROBENZENE BY PIPERIDINE FROM THE PHOTOPRODUCED [CHLOROBENZENE-PENTACARBONYLCHROMIUM(0)] SOLVATE

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Upon flash photolysis in chlorobenzene (CB) solution, $Cr(CO)_6$ reacts with piperidine (pip) to afford $(pip)Cr(CO)_5$. The reaction proceeds *via* photochemically-induced dissociation of CO and creation of specifically-solvated $[(CB)Cr(CO)_5]$. Studies in CB/hex (hex = hexanes) solutions indicate that displacement of CB by pip proceeds *via* a rapid solvation/desolvation pre-equilibrium and attack by pip at $[Cr(CO)_5]$. While the activation enthalpy for Cr–pip bond-fission is some 66.5. (29) kJ mol^{-1} greater than for Cr–CB bond-fission, the "competition ratios" of rate constants for pip and CB attack at the reacting intermediate to afford $[(pip)Cr(CO)_5]$ and $(CB)Cr(CO)_5$ at 13.8–35.4°C are 1.37(8) and are temperature-independent. Based upon data from previous studies, these results indicate that $[Cr(CO)_5]$ rather than $[(hex)Cr(CO)_5]$ is the intermediate which reacts with CB and pip. It also may be concluded that the enthalpy of activation for CB–Cr bond-fission, 41.0 (4) kJ mol^{-1}, closely approximates the CB–Cr bond-strength.

Keywords: Chromium, piperidine, chlorobenzene, Carbonyl complexes, Kinetics

INTRODUCTION

Studies of intermediate steps in ligand-exchange reactions of metal carbonyl complexes have centred on reactions of $Cr(CO)_6$. Of particular interest have been the influences of solvation on the reactivity of the solvated species produced after Cr–CO bond-fission (*1*).

$$\begin{tikzcd}
\mathrm{Cr(CO)_6} \arrow[r, "h\nu"] & {[\mathrm{Cr(CO)_5}]} \arrow[d, shift right, "k_{-1}[\mathrm{S}]"'] & \\
 & {[\mathrm{(S)Cr(CO)_5}]} \arrow[u, shift right, "k_1"'] \arrow[r, "\text{other steps}"] & \text{products}
\end{tikzcd} \tag{1}$$

(S = solvent)

Studies both in matrices and in solution have contributed to our understanding of these processes. A classic matrix isolation investigation by Perutz and Turner

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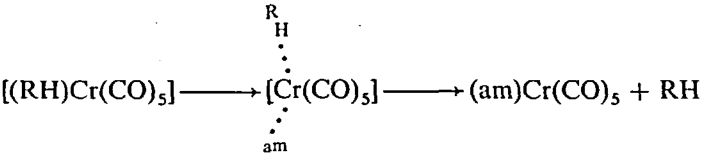
demonstrated that interactions of matrix molecules at the vacant coordination site in $[Cr(CO)_5]$ are specific and that their strengths depend strongly upon the identity of the "coordinating" molecule.[2] The latter conclusion has been supported by time-resolved studies of $[(S)Cr(CO)_5]$ transients produced after flash photolysis, which have shown that rates of desolvation (governed by $1-k_1$) are markedly different for hydrocarbons[3] and fluorocarbons.[4]

Energy changes accompanying the solvation process have also been studied. Yang, Peters and Vaida employed time-resolved photoacoustic calorimetry to estimate the strength of the C–H–Cr bond in $[(RH)Cr(CO)_4]$ (RH = *n*-heptane) to be *ca* 42 kJ mol^{-1}.[5] these workers have also found activation enthalpies for displacement of *n*-heptane by various amines (= am) from $[(n\text{-heptane})Cr(CO)_5]$ to be significantly smaller, results which they interpreted as indicative of an interchange process involving an R–H–Cr interaction in the transition state (*2*). On the other hand,



$$[(RH)Cr(CO)_5] \longrightarrow [\underset{\underset{am}{\vdots}}{\overset{\overset{R}{H}}{\overset{\vdots}{Cr}}}(CO)_5] \longrightarrow (am)Cr(CO)_5 + RH \qquad (2)$$

solvation of $[Cr(CO)_5]$ (governed by $1-k_{-1}$) takes place very rapidly. Thus, Simon and Xie have found the "rise-time" accompanying the interaction of methanol with $[Cr(CO)_5]$ to be 2.5 ps, while solvation of $[Cr(CO)_5]$ by cyclohexane is complete within the instrumental response time of 0.8 ps,[6] although the interpretation of these results has been questioned.[7] In the gas phase, the combination of CO with $[Cr(CO)_5]$ has been found to take place at rates which approach those calculated for the gas-kinetics reaction cross-section.[8] Thus, activation energies for solvation of

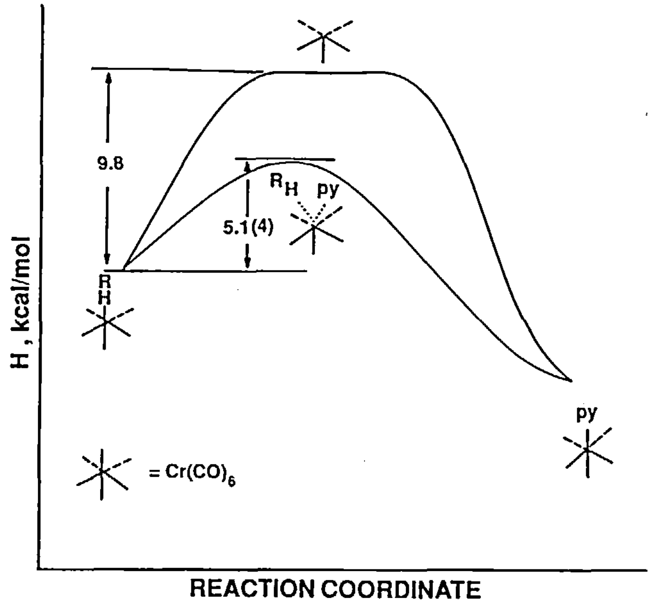


FIGURE 1 Plots of enthalpy *vs* reaction coordinate for reaction of $[(n\text{-heptane})Cr(CO)_5]$ with pyridine *via* a dissociative pathway (top), and *via* an interchange pathway (ref. 5).

$[Cr(CO)_5]$ are expected to approach zero, and, if the desolvation mechanism is dissociative, the microscopic reverse of the solvation process, rather than an interchange pathway, the strengths of the solvent–Cr bonds should closely approximate the activation energies for solvent–Cr dissociation. Figure 1 presents a potential energy *vs* reaction coordinate diagram which summarizes these possibilities for reactions of $[(n\text{-heptane})Cr(CO)_5]$ with pyridine (py).[5b]

We have been interested in studies of the mechanisms of displacement reactions of ligands ("solvents") much more weakly bonding than amines in order to probe mechanistic changes which may take place as the strengths of interaction of ligands and the metal atom decrease.[9] In view of the mechanistic possibilities for reactions of $[(\text{solvent})Cr(CO)_5]$ species as outlined above, the investigation of the kinetics and mechanism of reactions of $[(CB)Cr(CO)_5]$ produced after flash photolysis of $Cr(CO)_6$ in chlorobenzene (CB) solution with pip (=piperidine), (*3*), was undertaken for

$$Cr(CO)_6 \xrightarrow{h\nu} [(CB)Cr(CO)_5] \xrightarrow{+\,\text{pip}} (\text{pip})Cr(CO)_5 + CB \qquad (3)$$

comparison to the analogous reactions reported by Dennenberg and Darensbourg in which the more strongly binding pip is displaced from $(\text{pip})Cr(CO)_5$ in hydrocarbon solvent *via* a mechanism involving rate-determining fission of a Cr–pip bond.[10]

EXPERIMENTAL

Materials and syntheses

$Cr(CO)_6$ (Pressure Chemical) was purified by vacuum-sublimation. Chlorobenzene (Fisher) was fractionally distilled from P_4O_{10} under nitrogen. Hexanes (Fisher) were distilled from sodium under nitrogen. Piperidine (pip; Aldrich) was fractionally distilled from anhydrous KOH. The product produced after flash photolysis of $Cr(CO)_6$ in CB/pip solutions, $(\text{pip})Cr(CO)_5$, was synthesized and purified employing the method of Dennenberg and Darensbourg.[10]

Flash photolysis studies

Flash photolysis studies were carried out at the Center for Fast Kinetics Research (CFKR), University of Texas at Austin, employing a Quantel Model YG481 Nd-YAG laser operating in the frequency-tripled mode (355 nm); a 150 W xenon lamp was the analyzing source. Temperature control was maintained to ±0.1°C employing an external circulating bath and jacketted 1 cm quartz cell. Based upon time-resolved spectra taken after the flash (Fig. 2), 410 nm or 470 nm were taken as observation wavelengths. These spectra indicate that λ_{max} for the species produced after the flash ($[(CB)W(CO)_5]$, *vide infra*) is *ca* 480 nm, while λ_{max} for the reaction product is *ca* 420 nm. This last value corresponds well to λ_{max} for an authentic sample of $(\text{pip})Cr(CO)_5$ in CB solution (416 nm).

Each kinetics run, obtained employing $Cr(CO)_6$/CB/pip or $Cr(CO)_6$/CB/pip/hexanes solutions, was composed of the time-average of 5–10 flashes of the same solution. For the $Cr(CO)_6$/CB/pip/hexanes solutions the sums of the concentrations of CB and pip were held to less than 1 M to avoid rate effects which might accompany changing the nature of the reaction medium from one based predominantly on hexanes to one based predominantly on chlorobenzene.

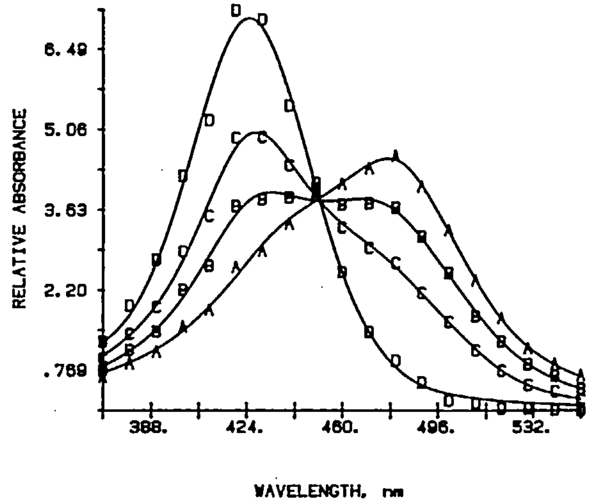


FIGURE 2. Plots of relative absorbance *vs* wavelength after flash photolysis of $Cr(CO)_6$ in piperidine/chlorobenzene solution (0.9775 M) at 24.5°C. Times after the flash, A: 1.0 μs; B: 13 μs; C: 32 μs; D: 134.5 μs. The data are fitted as a Gaussian/Lorentzian function.

It was determined that there were no significant differences between the traces obtained from the first and the last flash. That many flashes of a solution of $Cr(CO)_6$ in pip/CB solution afforded only $(pip)Cr(CO)_5$ (*i.e.*, that flash photolysis of $(pip)CR(CO)_5$ takes place exclusively *via* pip–Cr bond-fission), was confirmed from the electronic spectrum of a $Cr(CO)_6$/CB/pip solution recorded after many flashes, which showed absorptions attributable only to $Cr(CO)_6$ and $(pip)Cr(CO)_5$.

Rate constants and activation parameters obtained from the CFKR data were evaluated employing linear least-squares computer programs developed for our microcomputer. Limits of error for all data are given in parentheses as the uncertainty of the last digit(s) of the cited value to one standard deviation.

RESULTS

The time-resolved spectra obtained after flash photolysis of $Cr(CO)_6$ in a CB/pip solution (Fig. 2) show an absorption (λ_{max} *ca* 480 nm) produced immediately after the flash which is attributable to formation of $[(CB)Cr(CO)_5]$ as the predominant reaction species; it will be recalled that solvation of $[Cr(CO)_5]$ after its photochemical formation *via* flash photolysis takes place extremely rapidly.[6,7] The absorption at 480 nm is similar to that observed for $(pip)Cr(CO)_5$, but is shifted to lower energy (*ca* 480 nm *vs* *ca* 420 nm), consistent with a weaker interaction between CB and Cr than between pip and Cr.[2] There is much evidence which indicates that RX molecules interact with transition metal atoms *via* "normal" halogen-to-metal coordinate bonds.[11] Thus there is every reason to suppose that ligand-to-metal bonding in $[(CB)Cr(CO)_5]$ is analogous to that in $(pip)Cr(CO)_5$. The $[(CB)Cr(CO)_5]$ thus produced decays to afford $(pip)Cr(CO)_5$, identified through comparison of the electronic spectrum at long reaction times to that observed for an authentic sample of $(pip)Cr(CO)_5$ (λ_{max} = 416 nm; Figure 2). The isosbestic point observed in Figure 2 also indicates that (pip)Cr$(CO)_5$ is the only product formed through the decay of [(CB)Cr$(CO)_5$]. Thus the reaction stoichiometry accompanying flash photolysis is that shown in (3).

Initial rate studies of reactions of [(CB)Cr$(CO)_5$] produced after flash photolysis of Cr$(CO)_6$ were carried out in pure CB containing various concentrations of pip. Figure 3 illustrates a plot of the pseudo-first-order rate constants, k_{obsd}, *vs* [pip] taken at 31.1°C which indicates the reaction to obey the rate law (*4*).

$$-d[(CB)Cr(CO)_5]/dt = k[(CB)Cr(CO)_5][pip] \qquad (4)$$
$$k_{obsd} = k[pip].$$

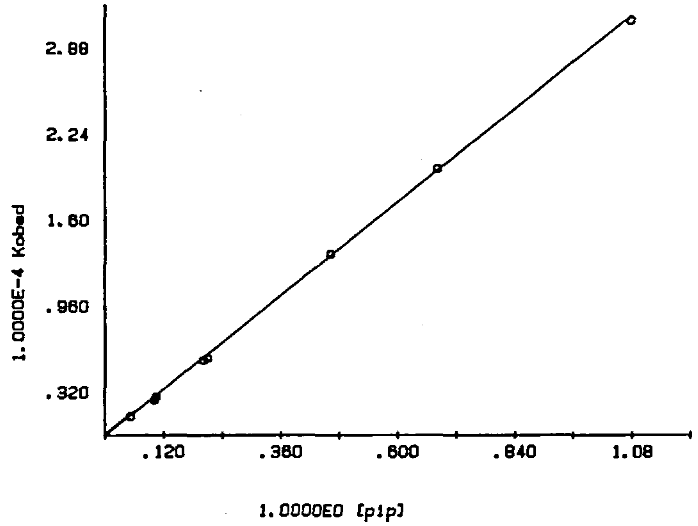


FIGURE 3. Plot of k_{obsd} *vs* [pip] for the reaction taking place after flash photolysis of Cr$(CO)_6$ in piperidine/chlorobenzene solution at 31.1°C.

To obtain further mechanistic information, studies in which the concentrations of CB could be varied were also carried out. Such studies are possible in CB/pip/hexanes solutions (hexanes = hex), since on the time-scale of this study [(hex)Cr)$CO)_5$] species are steady-state intermediates. The values of k_{obsd} obtained from rate studies of reactions of [(CB)Cr$(CO)_5$] in CB/pip/hex solutions at three temperatures are given in Supplementary Table I.* Plots of k_{obsd} *vs* [pip]/[CB] which obey the rate law,

$$k_{obsd} = k'[pip]/([CB] + k''[pip]) \qquad (5)$$

are exhibited in Figure 4. Equation (*5*) can be arranged to

$$1/k_{obsd} = k''/k' + [CB]/k'[pip]) \qquad (6)$$

for which plots of $1/k_{obsd}$ *vs* [CB]/[pip] are expected to be linear. These plots are shown in Figure 5. Values for the rate constants k' and k", as well as for k'/k"

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*These data are available from the Editor upon request.

(*vide infra*), obtained from plots of $1/k_{obsd}$ *vs* [CB]/[pip], together with activation parameters derived from them for data at three temperatures, are given in Table I.

TABLE I
Rate constants and activation parameters for the reactions taking place after flash photolysis of $Cr(CO)_6$ in piperidine/chlorobenzene/hexanes solution at various temperatures.

T/°C	$10^{-4}k_1k_2/k_{-1}$ $(=10^{-4}k')$ (s^{-1})	$10^{-4}k_1$ $(=10^{-4}k'/k'')$ (s^{-1})	k_2/k_{-1} $(=k'')$
13.8	5.65(13)	4.41(19)	1.28(9)
24.5	12.6(3)	8.6(4)	1.47(9)
35.4	21.2(3)	15.8(6)	1.35(7)

$\Delta H_1^\ddagger + \Delta H_2^\ddagger - \Delta H_{-1}^\ddagger = 42.7\ (33)\ \mathrm{kJ\,mol^{-1}}$; $\Delta S_1^\ddagger + \Delta S_2^\ddagger - \Delta S_{-1}^\ddagger = 0.0\ (84)\ \mathrm{J\,K^{-1}\,mol^{-1}}$.
$\Delta H_1^\ddagger = 41.0\ (4)$ kcal/mol; $\Delta S_1^\ddagger = -12.1\ (17)\ \mathrm{J\,K^{-1}\,mol^{-1}}$.
$\Delta H_2^\ddagger - \Delta H_{-1}^\ddagger = 1.7\ (38)\ \mathrm{kJ\,mol^{-1}}$; $\Delta S_2^\ddagger - \Delta S_{-1}^\ddagger = 10\ (10)\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

DISCUSSION

The rate behaviour observed for the reaction of $[(CB)Cr(CO)_5]$ in pure CB (*4*) can reasonably be attributed to either of two mechanisms. The first of these involves the displacement of CB by pip *via* a seven-coordinate activated complex, **7a**, (*7*),

$$\begin{tikzcd}
{[(CB)Cr(CO)_5]} \arrow[r, "k", "+pip"'] & {[(pip)(CB)Cr(CO)_5]^{(\ddagger)}\ \text{(a)}} \arrow[d, "fast"] \\
 & (pip)Cr(CO)_5 + CB
\end{tikzcd} \qquad (7)$$

The second mechanism envisaged is a dissociative process involving a rapid equilibrium between $[(CB)Cr(CO)_5]$ and the five-coordinate species $[Cr(CO)_5]$, followed by attack by pip at the latter, (*8*).

$$\begin{tikzcd}
 & {[(CB)Cr(CO)_5]\ \text{(b)}} \arrow[d, shift right, "k_1"'] \\
Cr(CO)_6 \arrow[r, "h\nu"] & {[Cr(CO)_5]} \arrow[u, shift right, "k_{-1}[CB]"'] \arrow[d, "\text{(a)}\ k_2[pip]"] \\
 & (pip)Cr(CO)_5
\end{tikzcd} \qquad (8)$$

Assuming a steady-state concentration of $[Cr(CO)_5]$, the rate law corresponding to (*8*) is

$$-d[(8-b)]/dt = k_1k_2[(8-b)][pip]/(k_{-1}[CB] + k_2[pip]) \tag{9}$$

for which the pseudo-first-order rate constants, k_{obsd}, obey the relationship

$$k_{obsd} = k_1k_2[pip]/(k_{-1}[CB] + k_2[pip]), \tag{10}$$

or, upon rearrangement, (*11*).

$$1/k_{obsd} + k_{-1}[CB]/k_1k_2[pip] \tag{11}$$

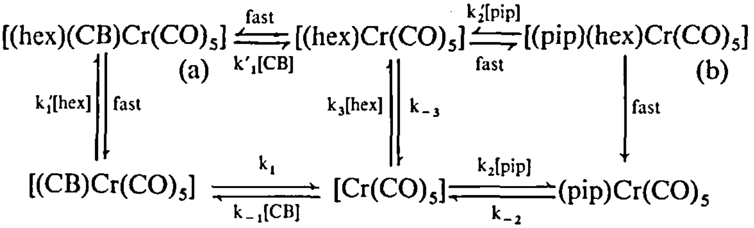
Since $[CB] \gg [pip]$, it is not unreasonable to presume that $k_{-1}[CB] \gg k_2[pip]$, whereupon (*11*) becomes (*12*)

$$k_{obsd} = k_1k_2[pip]/k_{-1}[CB] \tag{12}$$

The mechanism given in (*8*) is consistent with that observed for displacement of CB from *cis*-[(CB)(L)W(CO)$_4$] (L = P(O-*i*-Pr)$_3$ by pip.[13]

SCHEME 1

PATH B



PATH A

To obtain further mechanistic information, studies in which $k_{-1}[CB]$ and $k_2[pip]$ are competitive were carried out. Such studies are possible in CB/pip/hex solutions, in which the concentrations of CB can be varied widely. In these systems, for the dissociative mechanism (*8*), [(hex)Cr(CO)$_5$] will be present as steady-state intermediates since the observed rate constants for displacement of hex from [(hex)Cr(CO)$_5$] are more than three orders of magnitude greater than is that for displacement of CB from [(CB)Cr(CO)$_5$][12] and the [(hex)Cr(CO)$_5$] formed immediately after photolysis will have largely disappeared by the time the decay of [(CB)Cr(CO)$_5$] is monitored.

The use of hex as an "inert" solvent raises yet another mechanistic possibility, namely that [(CB)Cr(CO)$_5$] and (pip)Cr(CO)$_5$ are formed *via* interchange processes from [(hex)Cr(CO)$_5$]; this possibility, illustrated in Scheme 1, affords a rate law, (*B*),

$$k_{obsd} = (k'_1k'_2[pip]/(k'_{-1}[CB] + k'_2[pip]))[hex] \tag{13}$$

of the same form as (*10*). This mechanism, which envisages significant Cr–hex interaction in the transition state (Scheme 1, path b), *via* an "agostic" hydrogen,[14] is that proposed by Yang, Vaida and Peters[5b] for displacement of *n*-heptane from [(*n*-

heptane)Cr(CO)$_5$] by various Lewis bases, including pyridine (py). They favoured an interchange mechanism based upon the observed differences between the calculated Cr–*n*–heptane bond-strength (41.0 kJ mol^{-1}) and the activation energy for displacement of *n*-heptane from this intermediate by, *e.g.*, py (21.3(17) kJ mol^{-1}; see Figure 1). The interchange transition state differs from that for the dissociative pathway only in its relationship to the reactants and products: the dissociative pathway envisages a "late" transition state, while the interchange pathway involves an earlier one in which there is both Cr–heptane bond-making and Cr–pip bond-breaking.

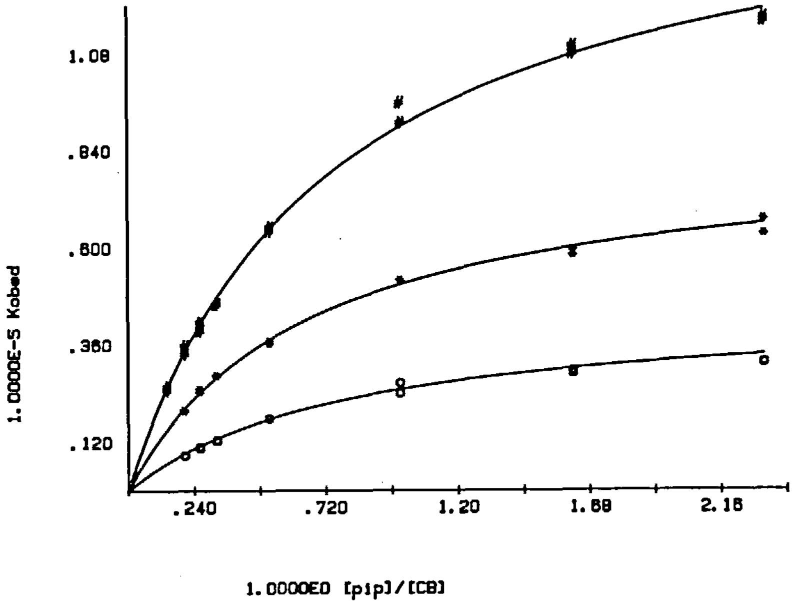


FIGURE 4. Plots of k_{obsd} *vs* [pip]/[CB] for the reaction taking place after flash photoloysis of Cr(CO)$_6$ in piperidine/chlorobenzene/hexanes solutions at various temperatures.

The values of k_{obsd} obtained from rate studies of reactions of [(CB)Cr(CO)$_5$] in CB/pip/hex solutions at three temperatures are given in Supplementary Table I. Plots of k_{obsd} *vs* [pip]/[CB] are exhibited in Figure 4; the corresponding plots of $1/k_{obsd}$ *vs* [CB]/[pip], which obey equation (*6*), are illustrated in Figure 5. The data support either mechanistic pathway shown in Scheme 1, since under the conditions employed for the reactions, [hex] $\gg$ ([pip] + [CB]) and thus [hex] is essentially constant.

We will presume for the moment that the applicable mechanism is that shown in path (a) of Scheme 1. If this is the case, from (*5*) and (*10*), $k' = k_1k_2/k_{-1}$, $k'' = k_2/k_{-1}$, the "competition ratios" of the rate constants for attack at [Cr(CO)$_5$] by pip and CB, respectively, and $k'/k'' = k_1$, the rate constant for dissociation of CB from [(CB)Cr(CO)$_5$]. These rate constants, together with the corresponding activation parameters, are given in Table I. As is shown in that table, the "competition ratios" are independent of temperature. Thus, $\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_{-1}$ is zero within experimental error (1.7 (38) kJ mol^{-1}). This value may be compared to the corresponding difference in ΔH^{+} for the reverse processes, for dissociation of pip from (pip)Cr(CO)$_5$, governed by k_{-2}, (Scheme 1), 107.5 (25) kJ mol^{-1},[10] and for dissociation of CB from $[(CB)Cr(CO)_5]$, governed by k_1 (Scheme 1), 41.0 (4) kJ mol^{-1} (Table 1). Thus, $\Delta H^{\ddagger}_2 - \Delta H^{\ddagger}_1$ is 66.5 (29) kJ mol^{-1}, and the strengths of Cr–pip and Cr–CB bonds differ very significantly, while the rates of attack by these ligands at the intermediate, whatever its identity, are virtually the same. From data extrapolated to 35°C, k_1/k_{-2} is *ca* 5×10^9, while $k_2/k_{-1} = 1.37$ (8). These data are consistent with the previously-demonstrated lack of selectivity of $[Cr(CO)_5]$ among incoming nucleophiles,[7,15] and thus strongly indicate that $[Cr(CO)_5]$ rather than $[(hex)Cr(CO)_5]$ is the reactive intermediate and favour a dissociative rather than an interchange process for the displacement of alkanes from $[(alkane)Cr(CO)_5]$ complexes. For an interchange process, some selectivity on the part of $[(hex)Cr(CO)_5]$ between pip and CB would be expected given the very large difference observed between the strengths of the pip–Cr and CB–Cr bonds being formed in the transition states. The ratios of rate constants, k_1k_2/k_{-1}, (k′, (*6*)), in hex solution and in CB solution, obtained as $k_{obsd}[CB]/[pip]$, (*11*), are 1.26 $(3) \times 10^5\ s^{-1}$ and 1.97 $(2) \times 10^5\ s^{-1}$, respectively. Thus the overall rates of CB displacement from $[(CB)Cr(CO)_5]$ by pip are quite similar in the two solvents.

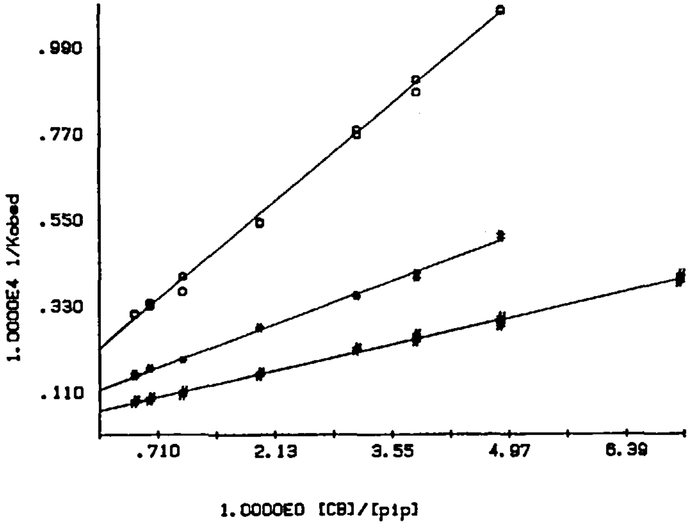


FIGURE 5. Plots of $1/k_{obsd}$ *vs* [CB]/[pip] for the reaction taking place after flash photolysis of $Cr(CO)_6$ in piperidine/chlorobenzene/hexanes solutions at various temperatures.

The enthalpy of activation for dissociation of CB from $[(CB)Cr(CO)_5]$ is 41.0 (4) kJ mol^{-1}, which should very closely approximate the Cr–CB bond-strength. The entropy of activation, -12.1 (17) J K^{-1} mol^{-1}), well within the range of entropies of activation for dissociative reactions of $LCr(CO)_5$ complexes (+138 to -59 J K^{-1} mol^{-1}),[16] compares closely to $\Delta S^{\ddagger}$ observed for dissociation of pip from $(pip)Cr(CO)_5$, 15.9 (79) J K^{-1} mol^{-1}.[10]

The availability of enthalpy data for dissociation of CB from $[(CB)Cr(CO)_5]$ and also for dissociation of pip from $(pip)Cr(CO)_5$ allows a correlation to be attempted between these data and the lowest energy electronic absorptions observed in $[(CB)Cr(CO)_5]$ and $(pip)Cr(CO)_5$, which have been attributed to $e(d_{xz}, d_{yz}) \rightarrow a_1(d_{z^2})$

($^1A_1 \rightarrow {}^1E$) transitions.[2,17] The a_1 orbital is raised somewhat in energy, upon coordination of the relatively weak base CB, and is raised still more upon coordination of pip, increasing the energy of this absorption, as is indicated by its shift from *ca* 480 nm ([(CB)Cr(CO)$_5$] in hex (Figure 2) to *ca* 420 nm, its position in a (pip)Cr(CO)$_5$/hex solution. The difference in the Cr–pip and Cr–CB bond strengths calculated from these absorptions, *ca* 71 kJ mol^{-1}, agrees well with the difference in the enthalpies of activation for dissociation of pip and CB from their LCr(CO)$_5$ complexes, 66.5 (29) kJ mol^{-1}.

It is to be noted that differences in the stabilities of the CB–Cr and pip–Cr bonds "need not be directly related to the separations of the visible bands",[2] since band positions also are influenced by the axial–radial bond angle in the pentacarbonylchromium group.[2,18] Changes in these angles have been observed, *e.g.*, in [(Ar)Cr(CO)$_5$] and [(Xe)Cr(CO)$_5$].[2] It is not however unreasonable to presume that the axial–radial bond angles in [(CB)Cr(CO)$_5$] and (pip)Cr(CO)$_5$ are quite similar, given the similar steric nature of CB and pip.

SUMMARY

The rate law observed for displacement of CB from [(CB)Cr(CO)$_5$] by pip indicates the mechanism to involve reversible CB–Cr bond-breaking followed by other rapid steps. The competition ratios for reactions of pip and CB with the transient ultimately produced after Cr–CB bond-breaking in [(CB)Cr(CO)$_5$] at various temperatures indicate that very little bond-making takes place in attaining the transition state leading to formation of either [(CB)Cr(CO)$_4$] or (pip)Cr(CO)$_5$. Thus, activation energies for ligand dissociation closely approximate the ligand–Cr bond-strengths, a result consistent with the positions in these complexes of electronic absorptions in the visible region.

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