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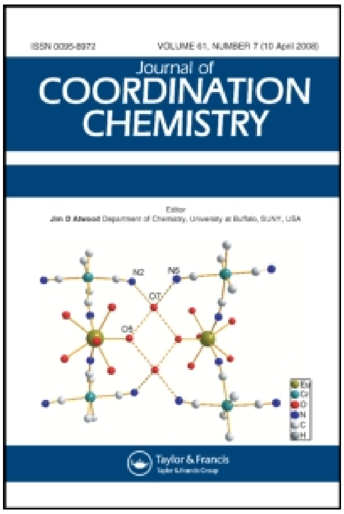

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MECHANISM OF DISPLACEMENT OF ALKANES FROM PHOTOGENERATED (ALKANE) $Cr(CO)_5$ COMPLEXES

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The kinetics and mechanism of displacement of *n*-heptane from (*n*-heptane)$Cr(CO)_5$ generated via pulsed laser flash photolysis in the presence of trapping nucleophiles, piperidine, tetrahydrofuran, pyridine, acetonitrile, 2-picoline, ethanol, 1-hexene, chlorobenzene and 2,6-lutidine) have been studied. Activation parameters suggest that the reactions take place via concurrent interchange and dissociative mechanisms, with the latter prominent where L_s is more sterically demanding. The lack of correlation between rate constants and activation parameters is interpreted to mean that for the dissociative pathway there is significant discrimination among the nucleophiles by $Cr(CO)_5$ produced via dissociation of *n*-heptane from (*n*-heptane)$Cr(CO)_5$. The results are discussed in terms of time-resolved photocalorimetric experiments reported for closely-related systems.

Keywords: Kinetics; chromium; metal carbonyl; flash photolysis; *n*-heptane

INTRODUCTION

Several studies have reported rates and mechanism for interaction of weak nucleophiles (L_w) such as alkanes with $Cr(CO)_5$ created by flash photolysis of $Cr(CO)_6$ in solution,[1]

$$Cr(CO)_6 \xrightarrow{h\nu} CO \rightleftharpoons [Cr(CO)_5] + L_w \longrightarrow (L_w)Cr(CO)_5 \qquad (1)$$

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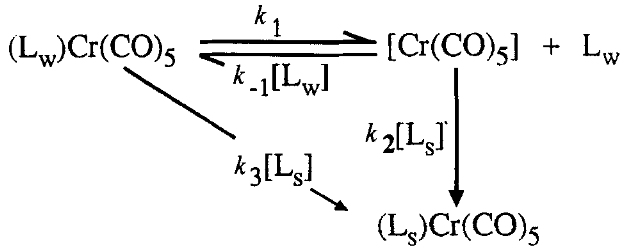
There also have been numerous reports of ligand-exchange in the $(L_w)Cr(CO)_5$ photolysis products in which L_w (alkanes, arenes, haloalkanes and haloarenes) are replaced by more strongly-bonding *trapping* nucleophiles, L_s, such as alkenes and amines,[2,3]

$$(L_w)Cr(CO)_5 + L_s \longrightarrow (L_s)Cr(CO)_5 + L_w \qquad (2)$$

These studies have had as their purpose the elucidation of the mechanism and energetics of these *ligand-exchange* reactions. For all of these studies, over a wide variety of L_w,[4] the observed rate behavior can be encompassed within an overall mechanism (3),



(3)

which exhibits competing dissociative (governed by k_1, k_2, k_{-1}) and interchange (governed by k_3) pathways. The contribution of each pathway to the overall mechanism has been found to be dependent on the identity of L_w and L_s.[2,3]

The displacement of a weakly-coordinating alkane ($= L_w$), *n*-heptane, which bonds to Cr through a –C–H–Cr three-center *agostic* interaction,[5] from photogenerated (*n*-heptane)$Cr(CO)_5$ intermediates by various L_s has been studied by Yang *et al.*, who presented time-resolved photoacoustic calorimetric (TRPAC) data for displacement of *n*-heptane from photogenerated (*n*-heptane)$Cr(CO)_5$ by various L_s bonding through O, N and P coordinate covalent bonds, or through a π-olefinic interaction.[6] Second-order rate constants, k_{2nd}, obtained through deconvolution of their data, were reported. Under the reaction conditions employed ([*n*-heptane] $\gg [L_s]$) and based on Equation 4, Equation 5 may be derived,

$$\begin{aligned}&-\mathrm{d}[(n\text{-heptane})Cr(CO)_5]/\mathrm{d}t\\&\quad = (k_1k_2/k_{-1}[n\text{-heptane}] + k_3)[(n\text{-heptane})Cr(CO)_5][L_s], \qquad (4)\end{aligned}$$

$$k_{2nd} = (k_1k_2/k_{-1}[n\text{-heptane}] + k_3)[L_s];\ k_{obsd} = k_{2nd}/[L_s]. \qquad (5)$$

Considering a single reaction pathway, the rate data of Peters *et al.* together with activation parameters they obtained for L_s = pyridine and

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2-picoline, led them to suggest that the transition state for Cr–L_w bond-breaking entailed "a high degree of heptane–Cr bond-lengthening concurrent with the association of the incoming ligand".[6] These workers also observed very significant differences in k_{2nd} as a function of the identity of L_s, also consistent with an interchange mechanism.[6] Their data would appear at first glance to be inconsistent with the dissociative pathway governed by k_1, k_2 and k_{-1} in view of the very rapid (ps–fs time scale) rate of interaction of alkanes with photogenerated $Cr(CO)_5$.[1] These extremely fast rates are suggestive of a very low activation barrier for interaction of L_w with $Cr(CO)_5$ (Equation 1), with little consequent discrimination among L_w with $Cr(CO)_5$, and *competition ratios*, k_2/k_{-1}, which thus are predicted to approximate 1.

The data of Peters *et al.* showed a variation of k_{2nd} of nearly ten-fold between L_s = acetonitrile and 1-hexene, which prompted us, through detailed kinetics studies, to compare rate data for $Cr(CO)_6/L_w/L_s$ systems for L_w = 1-chlorobutane (BuCl) and these two L_s.[3,7] The results obtained indicated that for L_s = 1-hexene an exclusively dissociative ligand-exchange takes place, but that for acetonitrile, both dissociative and interchange mechanisms were operative (Equation 3). Moreover, the overall differences in rate observed for the two systems were largely derived from differences in the *competition ratios* for the dissociative pathway, rather than from differences in nucleophilicity for L_s via the interchange pathway.[3,7] These observations have provided insight into ligand-exchange data we acquired some time ago which extended and complemented the work of Peters *et al.*[6] In those studies, reported here, rate constants and activation parameters for displacement of *n*-heptane from photogenerated (*n*-heptane)$Cr(CO)_5$ were obtained for nine L_s by employing standard kinetic techniques rather than through deconvolution of TRPAC data.[6]

EXPERIMENTAL

Materials

$Cr(CO)_6$ (Pressure Chemical Co.) was vacuum-sublimed before use. The weak nucleophile, *n*-heptane, was obtained from Fisher Scientific and was fractionally distilled from Na over nitrogen. The trapping nucleophiles, L_s, were obtained from the sources listed and purified by fractional distillation under nitrogen from the reagents given: piperidine, 2-picoline, Aldrich, Na; tetrahydrofuran (THF), Baker, Na; acetonitrile, Fisher, CaH_2; ethanol, Mc Cormick Distilling, CaH_2, stored over Linde 4A molecular sieves; 1-hexene, Aldrich, $MgSO_4$; chlorobenzene, Aldrich, P_2O_5; 2,6-lutidine, Lancaster, KOH; benzene, Mallinckrodt, Na.

Kinetics Studies

Flash photolysis data for reactions obeying Equation 2 were obtained at the Center for Fast Kinetics Research (CFKR), University of Texas at Austin, by employing a Quantel YG481 Q-switched Nd:YAG laser (third harmonic, 355 nm, 11 ns fwhi, 100 mJ maximum energy output), a pulsed 150 W Xe analyzing light source coupled to a Hammamatsu R928 pmt and a Biomation 8100 transient digitizer. The reaction sample was contained in a 1 cm jacketted quartz cuvette, and temperature was regulated through use of an external circulating thermostat (±0.05°C).

Solutions ca. 3.5×10^{-3} M in $Cr(CO)_6$ were employed. Since concentrations of L_s were low (0.01–0.3 M) as a consequence of operation near the time-resolution of the instrumentation, a $Cr(CO)_6$/*n*-heptane *blank* solution was also photolyzed to ascertain the influence of impurities on rate. This influence was found to be unimportant, since the value for the rate constant, k_{obsd} (Equation 4) was found to be within two standard deviations of zero. Plots of absorbance vs. time from monitoring 510 or 520 nm, exhibited exponential decay (Figure 1). Values of k_{obsd} were obtained from averages of 1–10 traces of plots of $\ln(A_t - A_\infty)$ vs. time, where A_t and A_∞ are

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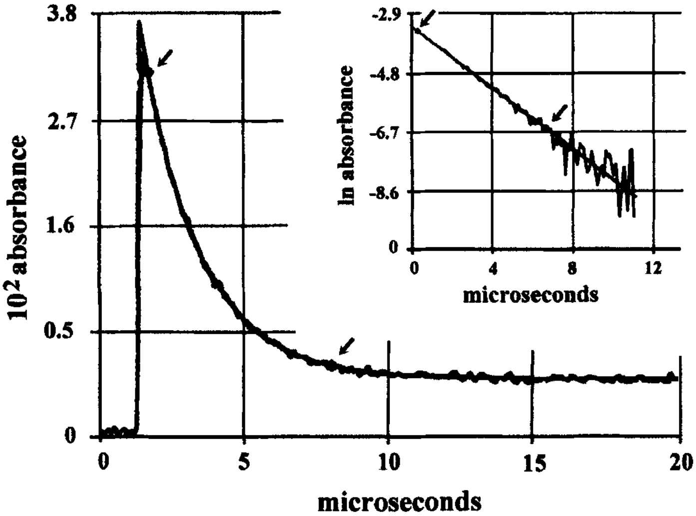

FIGURE 1 Plot of absorbance vs time for the reaction after flash photolysis of a $Cr(CO)_6$/*n*-heptane/1-hexene solution (0.0203 M) at 25°C. (*Inset*) plot of ln absorbance vs time for this reaction. The arrows indicate the portion of the plots taken for analysis.

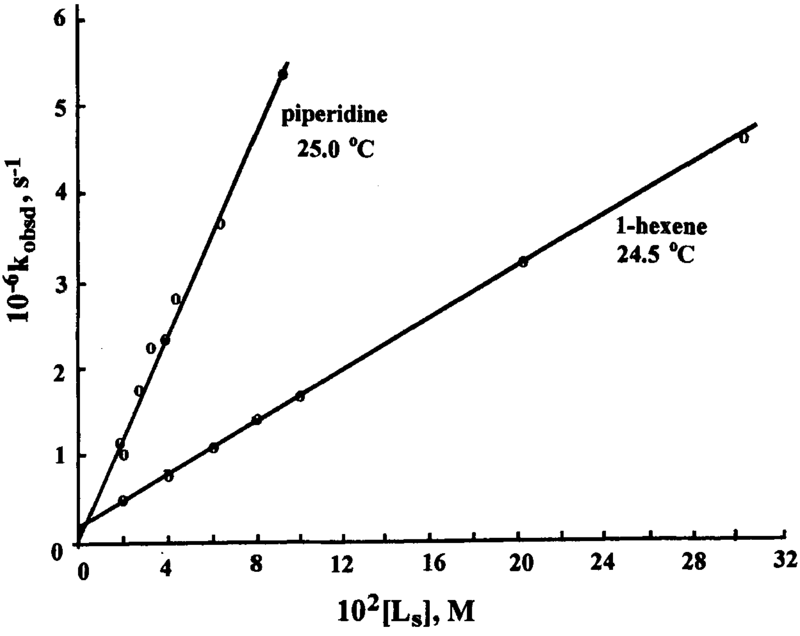

FIGURE 2 Plots of k_{obsd} vs $[L_s]$ after flash photolysis of $Cr(CO)_6$/*n*-heptane/L_s solutions (L_s = 1-hexene, piperidine) at near ambient temperature.

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measured absorbances at time *t* and at infinite time, respectively. These plots were found to be linear to several half-lives (inset, Figure 1) indicating that *pseudo* first-order reaction conditions were operative. Wherever signal-to-noise ratios for plots were relatively small, several independent time-averaged data sets were taken under identical reaction conditions, and the reported values of k_{obsd} are averages of those values. The kinetics data were analyzed by employing computer programs developed at CFKR. Values of k_{obsd} are given in the supplementary material; values of k_{2nd} were obtained by employing Equation 5. Plots of k_{obsd} vs. $[L_s]$ for piperidine and 1-hexene at near-ambient temperatures are given in Figure 2. Activation parameters were obtained from data taken over the temperature range of 1–46°C. Error limits, given in parentheses as the uncertainties of the last digit(s) of the cited value, are one standard deviation.

DISCUSSION

Table I presents values of k_{2nd} at 25°C for displacement of *n*-heptane from photogenerated $(hep)Cr(CO)_5$ by ten L_s. For the four L_s which are common

TABLE I Second-order rate constants, k_{2nd} (25°C), and activation parameters for photogenerated (n-heptane)Cr(CO)$_5$ complexes with various nucleophiles (L_s)

L_s	$10^{-7} k_{2nd}$ M^{-1} s^{-1}	k_{rel}[a]	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ cal/K mol
Piperidine	5.4(1)	3.7(1)	3.1(5)	− 12.5(16)
THF	11.8(4)	8.0(3)	4.1(2)	− 7.8(6)
Pyridine[b]	19.9(5)	13.5(4)	4.8(1)	− 4.3(4)
Acetonitrile	32(1)	21.9(7)	5.0(6)	− 3(2)
1-picoline[b]	9(2)	7.5(14)	6.1(5)	− 1.2(18)
Ethanol	7.0(2)	4.76(17)	6.6(13)	− 1(4)
1-hexene	1.47(1)	1.0	7.5(1)	− 0.3(4)
Chlorobenzene	3.2(3)	2.2(2)	7.5(1)	+ 1.4(3)
2,6-lutidine	8.0(7)	5.4(5)	7.9(8)	+ 4(3)

[a] The ratio of k_{2nd} for a given L_s vs that for 1-hexene.

[b] Activation parameters (Ref. [7]); pyridine: $\Delta H^{\ddagger} = 5.1(4)$ kcal/mol; $\Delta S^{\ddagger} = -3.2(14)$ cal/K mol; picoline: $\Delta H^{\ddagger} = 7.3(8)$ kcal/mol; $\Delta S^{\ddagger} = 2.6(28)$ cal/K mol.

in this study and that of Peters *et al.*[5] the values of k_{2nd} agree within a factor of 2, reasonable agreement considering the different methods employed to obtain them. The two common sets of activation parameters, for pyridine and 2-picoline, agree within one standard deviation (Table I).

The data in Table I are arranged in the order of decreasing values for $\Delta H^{\ddagger}$. It is to be noted that the values of $\Delta S^{\ddagger}$ increase regularly as $\Delta H^{\ddagger}$ values decrease ($R = 0.953$ for nine data sets), as expected in view of the values of k_{2nd}, which differ by less than a factor of 25. The variation in the activation parameters might suggest that the mechanism of displacement of n-heptane from (hep)Cr(CO)$_5$ changes along the series of L_s, with the interchange process decreasing and the dissociative pathway increasing in importance. If one presumes that the reactions (Equation 2) proceed exclusively via the dissociative pathway where the upper limit of the activation enthalpy is reached, ca. 8 kcal/mol, this value is in reasonable agreement with the Cr–n-heptane bond-energy, 11.6(26) kcal/mol, obtained by Burkey from TRPAC data.[8]

However, values of k_{2nd} show poor correlation with $\Delta H^{\ddagger}$ ($R = 0.398$). Based on the mechanism shown in Equation 3, this lack of correlation can arise only through variations in the competition ratios, k_2/k_{-1}, where these ratios are not correlated to the fraction of the reaction which proceeds via the interchange pathway. This conclusion is consistent with that drawn from the detailed kinetics studies for $L_s = $ 1-hexene, for acetonitrile in chlorobenzene, in which ten-fold differences in k_2/k_{-1} were observed.[3,7] Comparison of those data with the results obtained here also suggests that the interchange mechanism is more prominent for n-heptane than for chlorobenzene.

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The series, pyridine, 2-picoline, 2,6-lutidine, in which steric constraints at the coordinating nitrogen increase regularly, is of particular interest. The activation parameters suggest a regular shift from the interchange pathway to the dissociative pathway with increasing steric crowding at L_s. The relative constants, k_{rel} (Table I), also decrease along the series, consistent with decreases of k_2/k_{-1}, expected as L_s becomes bulkier. All the data can be interpreted as indicating that the contribution of the interchange pathway to the overall mechanism decreases with increasing steric demands of L_s. The dissociative pathway is surprisingly sensitive to the properties of L_s, which would indicate that nascent L_w–Cr interactions exist in the "$Cr(CO)_5$" intermediate.

Acknowledgments

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SUPPLEMENTARY MATERIAL

Values of k_{obsd} for the reactions (4 pages) are available from the corresponding author.

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