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Octahedral Metal Carbonyls
70.* Competitive Mechanisms for Displacement by 1-Hexene of n-Heptane from the Photogenerated $[(n\text{-Heptane})Cr(CO)_5]$ Transient

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Solvation/desolvation processes for $[(\text{alkane})Cr(CO)_5]$ molecules generated after laser flash photolysis have been the subject of much recent interest because these transient species are models for active intermediates in a number of important catalytic processes [1] and because the interaction of alkanes at the vacant coordination site (via an agostic hydrogen) [2] is the first step along the reaction coordinate to C–H bond activation by transition metal complexes [3]. We report data which indicate that replacement by 1-hexene of n-heptane (hep) from $[(\text{hep})Cr(CO)_5]$ produced after pulsed laser flash photolysis takes place by competitive associative and dissociative pathways.

The displacement of hep by a variety of nucleophiles (L, eqn. (1)) has been studied by Peters *et al.* employing time-resolved photoacoustic calorimetry

$$[(\text{hep})Cr(CO)_5] + L \longrightarrow (L)Cr(CO)_5 + \text{hep} \qquad (1)$$

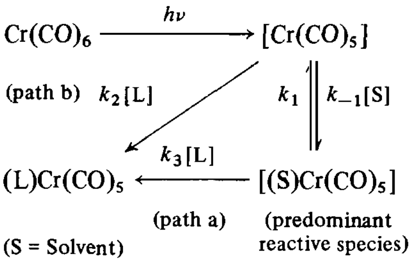
[4, 5] and by conventional laser flash photolysis [5]. Their data afford a second-order rate law

$$-d[(\text{hep})Cr(CO)_5]/dt = k[(\text{hep})Cr(CO)_5][L] \qquad (2)$$

where

$$k_{obs} = k[L] \qquad (3)$$

Other studies have indicated that $[Cr(CO)_5]$ reacts with L at rates for which $\Delta G^{\ddagger}$ approaches zero both in the gas phase [6] and in solution [7]; thus, based on Hammond's postulate [8], $[Cr(CO)_5]$ should not discriminate significantly among incoming nucleophiles. The results of Peters *et al.* [5], however, indicate considerable selectivity by the reactive intermediate produced after laser flash photolysis of $Cr(CO)_6$ in hep. Moreover, enthalpies of activation which vary with L and which are significantly smaller than the experimentally determined Cr–hep bond strength, and near-zero entropies of activation for reactions of $[(\text{hep})Cr(CO)_5]$ with L (eqn. (1)) are consistent with significant bond making in the transition state leading to solvent replacement [5]. These results suggest an associative reaction (Scheme 1, path a) rather than one in which L reacts with $[Cr(CO)_5]$ produced after hep dissociation from $[(\text{hep})Cr(CO)_5]$ (Scheme 1, path b). In contrast, in chlorobenzene (CB) solution, evidence suggests that desolvation of CB from the photogenerated $[(\text{CB})Cr(CO)_5]$ transient takes place via initial dissociation of CB (Scheme 1, path b) [9]. Thus, both mechanisms illustrated in Scheme 1 have been implicated in solvent-displacement reactions of $[(S)Cr(CO)_5]$ species (S = solvent). If these mechanisms are competitive, the pseudo-first-order rate law based on Scheme 1 ($[Cr(CO)_5]$ is a steady-state intermediate) is



Scheme 1.

$$k_{obs} = \{k_1k_2/(k_{-1}[S] + k_2[L]) + k_3\}[L] \qquad (4)$$

Where $[S] \gg [L]$ with $[Cr(CO)_5]$ relatively nondiscriminating between S and L (*vide supra*)

$$k_{obs} = \{(k_1k_2/k_{-1}[S] + k_3\}[L] \qquad (5)$$

i.e. a rate law consistent with that observed experimentally (eqn. (2)) since at low [L], [S] will be relatively constant.

The possible presence of the two terms in eqn. (5) (S = hep) has been explored through a comparison of the rate of hep displacement from $[(\text{hep})Cr(CO)_5]$ by hex in pure hep solvent versus that observed when this solution is diluted (1:1 vol./vol.) with MCH_f (= perfluoromethylcyclohexane). MCH_f interacts much less strongly with $[Cr(CO)_5]$ than does hep, as is indicated by the rate constants for displacement of MCH_f and hep from $[(S)Cr(CO)_5]$, $3.0(9) \times 10^9$ M^{-1} s^{-1} (L = cyclohexane) [10], versus $1.47(1) \times 10^7$ M^{-1} s^{-1} (L = hex at 25.0 °C), obtained in the present study†. Thus, $[(MCH_f)Cr(CO)_5]$ will be a

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†Pulsed laser flash photolysis studies were performed at the Center for Fast Kinetics Research, University of Texas at Austin, as described elsewhere (ref. 9). The monitoring wavelength was 520 nm, λ_{max} for $[(\text{hep})Cr(CO)_5]$. 1-Hexene was selected as a weak incoming nucleophile, for which a dissociative pathway for replacement of hep from $[(\text{hep})Cr(CO)_5]$ is more likely to be observed.

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steady-state intermediate in the presence of hep and, in the hep/MCH$_f$ solution

$$k'_{obs} = (k_1k_2/k_{-1})([L]/[hep]) + k_3[L]/2 \qquad (6)$$

Combination of eqns. (5) and (6) affords

$$2(k_{obs} - k'_{obs})/[L] = k_3 \qquad (7)$$

Thus, for a dissociative mechanism (k_3 = 0), k_{obs} = k'_{obs}, while for an associative mechanism (k_1k_2/k_{-1}[hep] = 0), k_{obs} = $2k'_{obs}$. For competing mechanisms $k_{obs} > k'_{obs} > k_{obs}/2$.

The dilution experiments were carried out using 1-hexene as the incoming nucleophile at 35.0 °C*. For [1-hexene] = 0.1188 M in pure hep (and half that concentration in 1:1 vol./vol. hep/MCH$_f$), k_{obs} (eqn. (5)) was determined to be 2.55(11) $\times 10^6$ s^{-1} and k'_{obs} to be 1.94(15) $\times 10^6$ s^{-1}, which correspond to a k_3 value of 1.0(4) $\times 10^7$ M^{-1} s^{-1} in pure heptane. Within experimental error, this rate constant indicates roughly equal contributions of the two reaction pathways to the overall rate, since k_1k_2/k_{-1}[hep] = 1.1(5) $\times 10^7$ M^{-1} s^{-1}; k_1k_2/k_{-1} = 8(3) $\times 10^7$ s^{-1}.

Eyring activation parameters for displacement of hep from [(hep)Cr(CO)$_5$] in pure hep by 1-hexene were determined from preliminary data over a temperature range of 2.0–45.0 °C. The enthalpy of activation, 7.4(1) kcal/mol, is not inconsistent with the value obtained for the hep–Cr bond strength (9.8 kcal/mol) by Peters *et al.* [4, 5] and with their conclusion for stronger nucleophiles such as pyridine that displacement of hep from [(hep)Cr(CO)$_5$] is (largely) associative in nature. The near-zero entropy of activation (0.6(4) cal/deg mol) also is consistent with competitive dissociative and associative reaction pathways observed here for L = hex.

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*These experiments were carried out at 35.0 °C rather than at 25.0 °C because MCH$_f$ and hep were observed not to be miscible at temperatures below 26.4(1) °C.