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Octahedral metal carbonyls

LXXII. Volumes of activation for solvent displacement in (solvent)$M(CO)_5$ transients (M = Cr, Mo, W) generated from $M(CO)_6$ via pulsed laser flash photolysis *

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Abstract

Pulsed laser flash photolysis of $M(CO)_6$ (M = Cr, Mo, W) in aliphatic and aromatic hydrocarbon solutions (solvent = n-C_7H_{16} and C_6H_5X (X = F, Cl, H, CH_3)) produces (solvent)$M(CO)_5$ transients, which then react with Lewis bases (L; 1-hexene, piperidine, 2-picoline, pyridine) to afford $LM(CO)_5$ products. The solvent-displacement process has been studied at variable pressures to 150 MPa, and volumes of activation for this process have been determined. These volumes of activation are sensitive to the identity of the coordinated solvent and suggest that bonding of chlorobenzene to Cr takes place via a lone pair of electrons on Cl, but through an isolated olefinic linkage for benzene, fluorobenzene and toluene. Observed volumes of activation also are consistent with the accessibility of an interchange mechanism for solvent displacement of n-heptane and with a dissociative solvent displacement mechanism for the arenes and support an increasing contribution from the solvent interchange process vs. reversible solvent dissociation in the order of the increasing size of the metal atom, Cr < Mo ≃ W. The observed ability of "$[M(CO)_5]$" to discriminate among various nucleophiles arises in part from the accessibility of these two competitive mechanisms.

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* For Part LXXI see ref. 1.

Introduction

Studies of solvent displacement by Lewis bases (L) from $(solv)Cr(CO)_5$ intermediates (solv = alkane, arene, substituted arene) produced after flash photolysis,

$$\begin{tikzcd} Cr(CO)_6 \arrow[r, "h\nu", "-CO"'] & {[Cr(CO)_5]} \arrow[r, "+solv"] & (solv)Cr(CO)_5 \arrow[d, "+L"] \\ & & LCr(CO)_5 \end{tikzcd} \qquad (1)$$

have been the subject of considerable controversy. Dissociative and "interchange" [2*] mechanisms, Eq. 2,

$$\begin{tikzcd} \underset{\mathbf{1}}{(solv)Cr(CO)_5} \arrow[r, shift left, "k_1"] \arrow[rd, "-solv", "k_3[L]"'] & {[Cr(CO)_5] + solv} \arrow[l, shift left, "k_{-1}"] \arrow[d, "k_2[L]"] \\ & LCr(CO)_5 \end{tikzcd} \qquad (2)$$

(path a)
interchange

(path b)
dissociative

have been implicated by the kinetics results. Under the conditions normally employed in kinetics studies, [solv] ≫ [L], these mechanisms are kinetically indistinguishable, since for the dissociative pathway (2b), where k_{-1} and k_2 are comparable,

$$-d[\mathbf{1}]/dt = (k_1k_2/k_{-1}[solv])[\mathbf{1}][L], \qquad (3)$$

while for the interchange pathway the anticipated rate law is,

$$-d[\mathbf{1}]/dt = k_3[\mathbf{1}][L]. \qquad (4)$$

Indirect means thus were employed initially to probe solvent-exchange mechanisms in these systems, through a comparison of solv–Cr bond strengths and the observed enthalpies of activation for solv–Cr bond-breaking. Peters, Vaida and Yang investigated solvent displacement from $(hep)Cr(CO)_5$ (hep = n-heptane) from the point of view of energetics. Employing time-resolved photoacoustic calorimetry, they have estimated the hep–Cr bond strength (bonding is through a C–H–Cr "agostic" [3] interaction) to be ca. 10 kcal/mol [4]. This result is in close agreement with a later study by Morse, Parker and Burkey for hep and several other alkanes [5]; that study also has afforded estimates of the hep–Mo and hep–W bond strengths, 8.7(27) and 13.4(28) kcal/mol, respectively. In contrast, Peters et al. have determined the enthalpies of activation for hep displacement from $[(hep)Cr(CO)_5]$ by pyridine and 2-picoline to be 5.1(4) and 7.3(8) kcal/mol, significantly less than the estimated strength of the hep–Cr bond (ca. 10 kcal/mol) [4]. The results of several research groups indicate that the microscopic reverse of hep dissociation, addition of hep to $[Cr(CO)_5]$, takes place very rapidly with a minimal enthalpic

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* Reference number with asterisk indicates a note in the list of references.

barrier [6]. Thus, for a mechanism involving reversible dissociation of hep from (hep)$Cr(CO)_5$ followed by attack by L at $[Cr(CO)_5]$, the observed enthalpy of activation should closely approximate the hep–Cr bond dissociation energy. Since this was not observed, Peters et al. concluded that the interchange mechanism (path 2a) was operative [4].

In further support of this conclusion, Peters and his associates also observed significant selectivity of hep displacement from (hep)$Cr(CO)_5$ by a variety of L [4]. Thus, for example, the rate of hep displacement by acetonitrile according to Eq. 1 was found to be some 25 times that of tri(n-butyl)amine. Further, entropies of activation of ca. zero determined for these exchange processes [4] are not inconsistent with an interchange mechanism for solvent displacement.

On the other hand, recent studies in chlorobenzene (CB) and in CB/hexanes (hex) solutions have provided evidence that displacement of CB by piperidine (pip) from (CB)$Cr(CO)_5$ involves rate-determining dissociation of CB and that in CB/hex mixtures, $[Cr(CO)_5]$ rather than (hex)$Cr(CO)_5$ is the species which reacts with pip [7]. Further, dilution studies of displacement of hep from (hep)$Cr(CO)_5$ by 1-hexene in hep/perfluoromethylcyclohexane solutions have provided data which suggest that both dissociative and interchange mechanisms are operative [8]. Another report has provided conclusive evidence that displacement of benzene (= bz) from photogenerated (η^2-bz)$Cr(CO)_5$ by pip or 1-hexene takes place via a dissociative pathway, although for L = pyridine, both dissociative and interchange pathways are accessible [1].

Volumes of activation have been found to be useful indicators of mechanism in a variety of contexts [9,10], and flash photolysis/variable pressure equipment which permits the evaluation of volumes of activation for systems such as those discussed above has been developed [11]. The present work reports volumes of activation for reactions proceeding according to Eq. 1 for $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ for several solvents (solv) and incoming nucleophiles (L) in order to obtain an overview of the mechanistic possibilities for solvent displacement in these systems.

Experimental section

Materials

$Cr(CO)_6$ and $W(CO)_6$ (Pressure Chemical Co.) and $Mo(CO)_6$ (Climax Molybdenum) were vacuum-sublimed before use. All solvents and ligands were distilled under nitrogen. The solvents n-heptane (hep), benzene (bz) and toluene (tol) (Mallinckrodt) were distilled from sodium, while fluorobenzene (FB) and chlorobenzene (CB; Aldrich Chemical Co.) were distilled from P_4O_{10}. Piperidine (pip; Aldrich) and 2-picoline (pic, Aldrich) and pyridine (py, Fisher) were distilled from KOH; 1-hexene (hex, Aldrich) was distilled from anhydrous $MgSO_4$.

Laser flash photolysis studies

Flash photolysis at variable pressure studies for all solvents except n-heptane were carried out employing a Lumonics TE-430 excimer laser (XeF; 351 nm; 14 ns fwhi), the beam from which was focussed upon a thermostated high pressure autoclave, which contained a "pill-box" optical cell [12] of pathlength ca. 15 mm; the high pressure apparatus has been described in detail elsewhere [13], as have other details of the flash photolysis equipment [14]. For n-heptane solutions, the studies were carried out at the Center for Fast Kinetics Research, University of Texas at Austin, using previously described [15] photolysis equipment and the pressure gear described above. In a typical flash photolysis experiment a 3 m*M* solution of the metal hexacarbonyl in solvent (solv) containing a sufficient excess of the "trapping" ligand, (L) was employed to insure that pseudo first-order conditions obtained. In all cases the observed rate constants were determined from averages of up to 10 traces obtained employing the same solutions and no significant differences were observed for traces obtained after a single flash or after several consecutive flashes. Data were analyzed employing programs developed in-house for our 286-based microcomputer. Limits of error for the data, given in parentheses as the uncertainties of the last digit(s) of the cited value, are one standard deviation. Pseudo first-order rate constants for individual kinetics runs at various pressures monitored at various wavelengths at 25.0 °C are presented in Supplementary Table 1 (available from the authors). Table 1 exhibits values of $\Delta V^{\ddagger}$ obtained from these data.

Results and discussion

Figure 1 exhibits typical time-resolved spectra, obtained after flash photolysis of $Cr(CO)_6$ in FB/pip solution (1.056 *M*). The inset shows the spectrum taken 1.7 μs after the flash, resolved into absorbances for $(FB)Cr(CO)_5$, $\lambda_{max} = 477(2)$ nm and $(pip)Cr(CO)_5$, $\lambda_{max} = 417(1)$ nm. These assignments are consistent with those reported in other studies [1,7,16]; in particular, that for $(pip)Cr(CO)_5$ is confirmed through its comparison with the visible spectrum for an authentic sample [1]. Figure

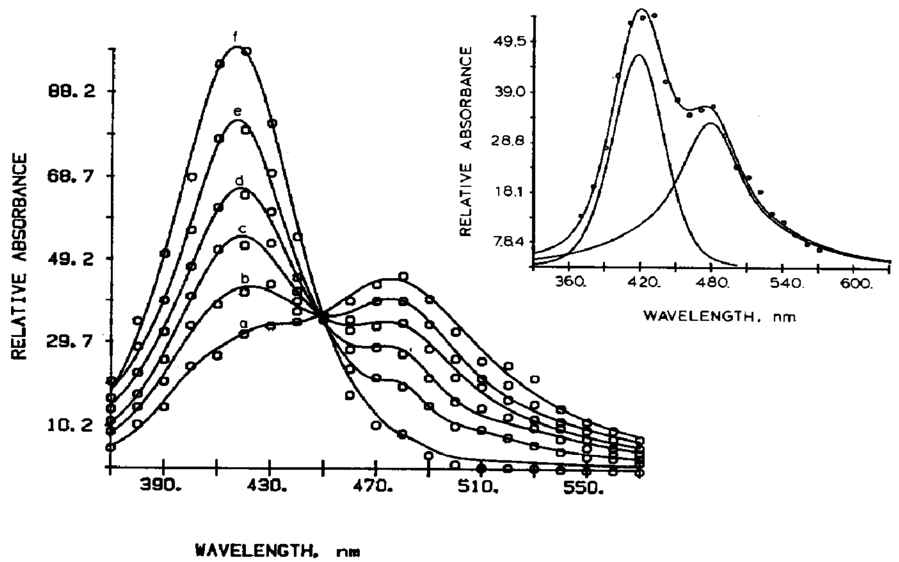

Fig. 1. Time-resolved spectra for the reaction taking place after flash photolysis of $Cr(CO)_6$ in a fluorobenzene/piperidine (FB/pip) solution (1.056 *M*). The spectra were obtained at the following times after the flash (μs): a, 0.4; b, 1.0; c, 1.7; d, 2.7; e, 4.45; f, 13.45. The inset shows the spectrum taken 1.7 μs after the flash resolved into absorbances for $(FB)Cr(CO)_5$, $\lambda_{max} = 477(2)$ nm and $(pip)Cr(CO)_5$, $\lambda_{max} = 417(1)$ nm.

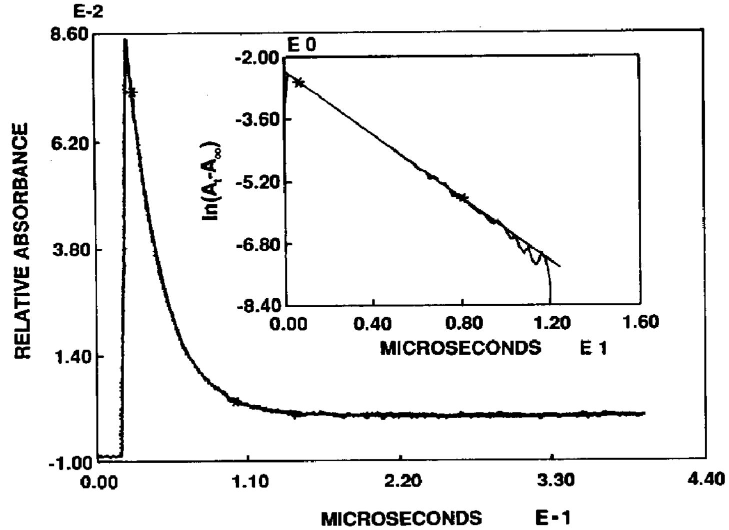

Fig. 2. Plot of absorbance (A) vs. time, monitoring at 490 nm, for the reaction taking place after flash photolysis of $Cr(CO)_6$ in a fluorobenzene/piperidine solution (1.550 M). The inset is a plot of $\ln(A_t - A_\infty)$ vs. time for those data.

2 shows a plot of absorbance vs. time monitoring 490 nm after flash photolysis of a 1.550 M pip/FB solution; the inset depicts a plot of $\ln(A_t - A_\infty)$ vs. time (A_t and A_∞ are absorbances at time t and at infinite time, respectively) which demonstrates that the reaction obeys pseudo first-order kinetics (solv = FB),

$$-d[(\mathrm{solv})\mathrm{Cr(CO)_5}]/dt = k_{\mathrm{obsd}}[(\mathrm{solv})\mathrm{Cr(CO)_5}] \tag{5}$$

From data (not shown) taken at several concentrations at ambient pressure where [pip] $\ll$ [FB], it was observed that,

$$k_{\mathrm{obsd}} = k[\mathrm{L}] \tag{6}$$

in this instance, L = pip. Analogous second-order rate laws were observed for all S and L [1,7,16]; thus all rate data can be encompassed within the overall mechanism shown in Eq. 2, for which the two reaction pathways obey the rate laws given in Eqs. 5 and 6 (cf. Eqs. 3 and 4). Therefore, based on Eq. 6,

$$k = k_1k_2/k_{-1}[\mathrm{solv}] + k_3 \tag{7}$$

Volumes of activation, determined from rate constants for reactions of photoproduced $(\mathrm{solv})\mathrm{M(CO)_5}$ intermediates with L at various pressures, are related by,

$$-RT(\partial \ln k/\partial P)_T = \Delta V^\ddagger, \tag{8}$$

and, where $\Delta V^\ddagger$ is independent of P,

$$\ln k = \mathrm{const.} - (\Delta V^\ddagger/RT)P. \tag{9}$$

Thus, employing Eqs. 6 and 9, plots of ln k vs. P should afford values of $\Delta V^\ddagger$.

Table 1 gives values of k and of $\Delta V^\ddagger$ at 25 °C for all the systems investigated. Values of $\Delta V^\ddagger$ were obtained from the slopes of plots of ln k vs. pressure. Representative examples of these plots, which are linear for pressures from ambient

Table 1

Rate constants and volumes of activation for solvent displacement from (solv)M(CO)$_5$ transients (M = Cr, Mo, W) by Lewis bases (L) at 25 ° C

M	Solvent	L	$10^{-5}\,k$ [a] ($M^{-1}\,s^{-1}$)	$\Delta V^{\ddagger}$ (cm^3/mol)
Cr	n-heptane	1-hexene	147(1)	+6.2(2)
		piperidine	540(10)	+1.4(4)
		2-picoline	900(220)	−1.4(3)
		pyridine	1990(50)	−1.4(5)
	fluorobenzene	1-hexene	0.889(3)	+9.4(7)
		piperidine	2.94(4)	+6.1(3)
		pyridine	7.0(5)	+8.2(2)
	chlorobenzene	1-hexene	0.0374(1)	+5.4(4)
		piperidine	0.222(2)	+0.2(2)
		2-picoline	0.181(1)	+3.1(6)
	benzene	1-hexene	0.091(2)	+10.9(10)
		piperidine	0.57(2)	+4.2(3)
	toluene	1-hexene	0.0506(6)	+10.8(7)
		piperidine	0.226(1)	+4.8(14)
Mo	n-heptane	1-hexene	158(1)	+2.2(3)
	fluorobenzene	1-hexene	0.178(7)	+5.8(8)
		pyridine	3.22(5)	+6.3(1)
	chlorobenzene	1-hexene	0.0509(6)	+3.2(3)
	toluene	1-hexene	0.00754(1)	+3.2(3)
W	n-heptane	1-hexene	15.8(5)	+2.7(4)
	fluorobenzene	1-hexene	0.00435(4)	+2.5(2)
	chlorobenzene	1-hexene	0.00138(1)	+0.4(3)

[a] At ambient pressure.

to 150 MPa *, are shown in Fig. 3. These data can be discussed in terms of the influence of the solvent, the incoming nucleophile and the identity of the metal atom.

Volumes of activation and the solvent

Noting that kinetics evidence strongly supports a dissociative pathway for displacement of solv from (solv)Cr(CO)$_5$ by pip where solv = bz [1], CB [7] and FB [16], based on Eq. 3, $k = k_1 k_2 / k_{-1}[\text{solv}]$, and $\Delta V^{\ddagger} = \Delta V^{\ddagger}(k_1) + \Delta V^{\ddagger}(k_2) - \Delta V^{\ddagger}(k_{-1})$, or $\Delta V(K_{\text{eq}}) + \Delta V^{\ddagger}(k_2)$, where $\Delta V(K_{\text{eq}})$ is the change in molar volume accompanying desolvation. This value is expected to be positive, since it involves release of a solvent molecule from the coordination sphere of (solv)Cr(CO)$_5$. For a given incoming nucleophile, $\Delta V^{\ddagger}(k_2)$ will not vary, and thus the change in $\Delta V^{\ddagger}$ will depend only upon $\Delta V(K_{\text{eq}})$. This value might increase with increasing molar volume of the solvent molecules employed, but such a trend is not evident for FB, bz and tol (Table 2), which also gives values of $\bar{V}$, the molar volumes, for S and L. It

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* Based upon Eq. 7 and the accessibility of two competitive pathways, these plots should be curved, since the change in pressure will alter the relative contributions of these pathways to the observed rate. However, the plots are linear within a standard deviation of 0.5 cm^3/mol, on the average, which indicates that the partitioning of the mechanism between the two competitive pathways does not change sufficiently over the pressure range employed to afford significant curvature.

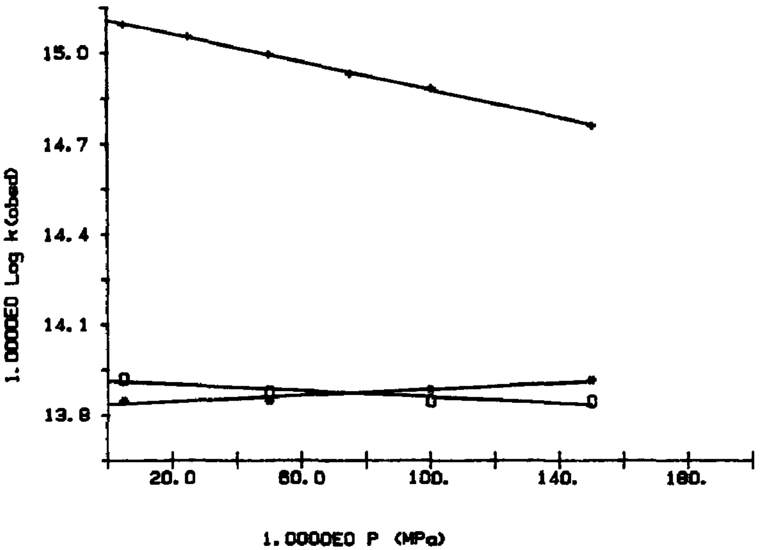

Fig. 3. Plots of ln k vs. pressure for reactions taking place after flash photolysis of $Cr(CO)_6$: +, n-heptane/1-hexene (0.240 M); ○, n-heptane/piperidine (0.01784 M); ★, n-heptane/picoline (0.01188 M).

is to be noted, however, that values of $\Delta V^{\ddagger}$ are significantly smaller, by 3–6 cm^3/mol, for CB and hep. The decrease is especially noteworthy for hep, since, if the solvent molar volumes influence $\Delta V^{\ddagger}$, the much larger $\bar{V}$ for hep than for the arene ligands might be expected to result in a more positive $\Delta V^{\ddagger}$.

It also is to be noted that the rate constants, k (Eq. 7; M^{-1} s^{-1}) for displacement of solv from $(solv)Cr(CO)_5$ by 1-hexene at 25 °C vary as follows: CB $(3.74(1) \times 10^3)$ < toluene $(5.06(6) \times 10^3)$ < benzene $(9.1(2) \times 10^3) \ll$ FB $(8.89(3) \times 10^4) \ll$ hep $(1.47(1) \times 10^7)$; the same trend is noted for pip. Thus arenes and substituted arenes are displaced much more slowly than is the alkane. Considering the series of XC_6H_5 solvates ($X = CH_3$, H, Cl, F), it is observed that rates of displacement of the arene do not correspond to the electron-releasing abilities of X [17], the displacement of CB being slower than would be anticipated on this basis. The observed trend may be attributable to a different mode of bonding of CB to the metal, via a Cl-to-Cr coordinate covalent bond, while benzene and toluene coordinate through a double bond of the arene.

Based only on the observed relative rates of solvent displacement, the mode of bonding of FB to Cr, whether through F or by means of a C=C interaction, is

Table 2

Volumes of activation for reactions of $(solv)Cr(CO)_5$ transients with 1-hexene and piperidine

Solvent, $\Delta V^{\ddagger}$ (cm^3/mol)					$\bar{V}$ (cm^3/mol)	L
FB	bz	tol	CB	hep		
9.4(7)	10.9(10)	10.8(7)	5.4(4)	6.2(2)	125.0	1-hexene
6.1(3)	4.2(3)	4.8(14)	0.2(2)	1.4(4)	98.9	pip
94.0	88.9	106.3	101.8	146.6	$\bar{V}$, solvent	

uncertain. However, volumes of activation are markedly less positive for CB than for the other three substituted arenes for both pip and hex as incoming nucleophiles, an observation which may indeed be related to differing modes of attachment to Cr of CB vs. the other three arenes, which thus might suggest bonding to Cr via C=C in FB as well. There is considerable evidence other than that presented here, in the form of X-ray crystallographic and other data, of the differing mode of attachment of substituted haloalkanes and haloarenes (X = Cl, Br, I) [18], via coordination of X to the transition metal vs. coordination "edgewise" through a C=C linkage in benzene and fluoroarenes [19].

Bonding of n-heptane to Cr is likely to take place via a two-electron three-center "agostic" C–H–Cr interaction [3]. In this regard it is to be noted (Table 2) that volumes of activation for the displacement of CB and hep from their $(solv)Cr(CO)_5$ transients are significantly smaller (ca. 3–6 cm^3/mol) than for the analogous solvates containing C_6H_5X ($X = CH_3$, H, F); this may suggest a smaller "collapse" in volume upon "head-on" Cl–Cr and C–H–Cr bond formation in the solvates than upon "edgewise" bonding of the arene to Cr via an olefinic linkage [1].

The decrease in $\Delta V^{\ddagger}$ noted from FB, bz and tol to CB and hep is especially noteworthy for hep, since, if the solvent molar volumes influence $\Delta V^{\ddagger}$, the much larger $\bar{V}$ for hep than the arene ligands might be expected to result in a more positive $\Delta V^{\ddagger}$ for hep than for CB. That values of $\Delta V^{\ddagger}$ for CB and hep are similar is consistent with the accessibility of an interchange solvent displacement pathway in the latter (see below) as is suggested by the studies of Peters and coworkers [4] and of Zhang and Dobson [8].

Volumes of activation and the incoming nucleophile

For M = Cr, volumes of activation for solvent displacement from $(solv)Cr(CO)_5$ employing 1-hexene as the "trap" are uniformly larger, by 3–7 cm^3/mol, than are those observed for pip (Table 2). Table 3 presents data for displacement of hep from $(hep)Cr(CO)_5$ by four L, which further indicates this trend that volumes of activation decrease with the decreasing molar volumes of the incoming nucleophiles. It thus is reasonable to presume that this trend arises at least in part as a consequence of differences in the molar volumes of L. However, Table 3 also presents rate constants for displacement of hep from $(hep)Cr(CO)_5$ as a function of the identity of the incoming nucleophile, together with the thermal activation parameters for hep displacement by pic and py as determined by Peters and coworkers [4]; thus, lower volumes of activation also may be correlated with increased rates of hep displacement and with the thermal activation parameters. These data thus might be

Table 3

Rate and activation data for reactions of $(n\text{-heptane})Cr(CO)_5$ transients with various Lewis bases (L)

L	$10^{-7}\,k$ [a] (s^{-1})	$\Delta V^{\ddagger}$ (cm^3/mol)	$\Delta H^{\ddagger}$ [b] (kcal/mol)	$\Delta S^{\ddagger}$ [b] (e.u.)	$\bar{V}$ (cm^3/mol)
hex	1.47(1)	+6.2(2)	–	–	125.0
pip	5.4(1)	+1.4(4)	–	–	98.9
pic	9.0(22)	−1.4(3)	7.3(8)	+2.6(28)	98.9
py	19.9(5)	−1.4(5)	5.1(4)	−3.2(14)	80.5

[a] Eq. 6. [b] Ref. 4.

Table 4

Volumes of activation and relative rates for reactions of (solv)$Cr(CO)_5$ transients with Lewis bases (L)

L	Solvent, $\Delta V^{\ddagger}$ [relative rate]			$\bar{V}$ (cm^3/mol)
	hep	CB	FB	
hex	6.2 [1]	5.4(1) [1]	9.4(7) [1]	125.0
pip	1.4(4) [4.7]	0.2(2) [5.9]	6.1(3) [3.3]	98.9
pic	−1.4(3) [6.1]	3.1(6) [4.8]	– –	98.9
py	−1.4(5) [13.5]	– –	8.2(6) [7.9]	80.5

interpreted in terms of an increasing contribution of the interchange process governed by k_3 (eq. 2) as the molar volumes of L decrease. This point is further explored through data presented in Table 4, which present volumes of activation and relative rates of solvent displacement for hep, CB and FB with four L. Since it has been demonstrated that displacement of CB and FB by L are dissociative in nature [7,16], the relative rates of solvent displacement by L in these solvents, which are similar from solvent to solvent, may be taken as a measure of the discriminating ability of [$Cr(CO)_5$] among the various L. It then is noteworthy that the apparent discriminating ability in hep for py is significantly greater than is observed in FB. This observation strongly suggests to us that the interchange pathway is operative in (hep)$Cr(CO)_5$. Thus, the apparent discriminating ability of (hep)$Cr(CO)_5$ likely arises in part from the accessibility of the interchange pathway in hep.

Volumes of activation and the metal atom

Table 5 illustrates changes in volumes of activation for reactions of various [(solv)$M(CO)_5$] intermediates (solv = FB, tol, CB, hep; M = Cr, Mo, W) with 1-hexene. Two trends are evident: the first is that values of $\Delta V^{\ddagger}$ decrease from Cr to Mo and W; the second is that differences noted between $\Delta V^{\ddagger}$ for FB and tol vs. CB and hep for the Cr solvates are not as noticeable for Mo and W.

The first trend, the decrease observed in $\Delta V^{\ddagger}$ from Cr to Mo and W, is most simply suggestive of an increasing influence of the interchange mechanism down Group VIB and is consistent with previous observations. Thus a recent study of chelate ring displacement by Lewis bases in (chelate)$M(CO)_4$ complexes (chelate = chelating ligand coordinating through S) has indicated that $\Delta V^{\ddagger}$ values decrease significantly from Cr to Mo, a trend interpreted to a change in mechanism for

Table 5

Volumes of activation for reactions of (solv)$M(CO)_5$ transients (M = Cr, Mo, W) with 1-hexene

M	Solvent, $\Delta V^{\ddagger}$ (cm^3/mol)				
	FB	tol	bz	CB	hep
Cr	9.4(7)	10.8(7)	10.9(10)	5.4(4)	6.2(2)
(pyridine)	8.2(6)	–	–	–	–
Mo	5.8(8)	3.2(3)	–	3.2(3)	2.2(3)
(pyridine)	6.3(1)	–	–	–	–
W	2.5(2)	–	–	0.4(3)	2.7(4)
(pyridine)	2.7(5)	–	–	–	–

rate-determining chelate ring-opening for Cr to chelate displacement by L for the larger Mo atom [20]. In CO displacement reactions of Group VIB metal carbonyls where the dissociative and interchange mechanisms are kinetically distinguishable, for reactions of $M(CO)_6$ [21] and $(phen)M(CO)_4$ [22] in particular, it also has been noted that the relative contribution of the interchange pathway increases in the order $Cr < Mo \simeq W$, the order of increasing atomic size, and related to the order of increasing effective nuclear charge ($Cr < Mo \ll W$) [23]. The larger atomic size of Mo and W also may explain the observed lack of differences in $\Delta V^{\ddagger}$ as a function of the identity of the solvent, differences noted for Cr (see above). Larger atomic size may be expected to diminish the steric discrimination of the metal atoms for coordinated solvent molecules.

Conclusions

The activation volumes data presented here are consistent with mechanistic interpretations which have been proposed for desolvation reactions of $(solv)Cr(CO)_5$ transients, favoring dissociative desolvation pathways for arene solvents and consistent with the accessibility of an interchange pathway for $(hep)Cr(CO)_5$. The results further demonstrate that volumes of activation observed for solvent displacement reactions from $(solv)M(CO)_5$ are sensitive to the identities of the incoming nucleophile and the metal atom. The results for $(solv)Cr(CO)_5$ suggest differing modes of bonding for CB, via a Cl–Cr coordinate bond, and for bz, FB and tol, through an interaction between Cr and an isolated olefinic linkage. The data also support the increasing importance of an interchange pathway for solvent displacement for Mo and W vs. Cr and, in $(hep)Cr(CO)_5$, with the decreasing molar volumes of L. It is concluded that varying contributions of the interchange pathway to rates observed for displacement of hep by L in $(hep)Cr(CO)_5$ transients is responsible in part for the observed selectivity of "$[Cr(CO)_5]$" among various L.

These results underscore the similarities between solvent-displacement mechanisms for $(solv)M(CO)_5$ transients and the hexacarbonyls and their substitution products.

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