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Notes

Volumes of Activation for Solvent Displacement Reactions on Pentacarbonylchromium(0). Comparison of Data for Pure and Mixed Solvents

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Summary: The solvent displacement reactions of $Cr(CO)_5S$ (S = fluorobenzene, *n*-heptane), prepared via flash photolysis of $Cr(CO)_6$ in these solvents, with piperidine were studied as a function of pressure for a wide concentration range of these solvents. The results confirm mechanistic conclusions reached on the basis of pure solvent studies and work at ambient pressure in mixed solvents. Displacement of fluorobenzene follows a dissociative mechanism, whereas the displacement of *n*-heptane takes place via competitive dissociative and interchange pathways.

Introduction

Solvent displacement reactions of group VIB metal carbonyl complexes of the type $M(CO)_5S$ (M = Cr, Mo, W) have received significant attention in recent years because of their importance with respect to the participation of highly reactive, coordinatively unsaturated $M(CO)_5$ species in catalytic cycles.[2-5] We have shown in earlier work that important mechanistic information on such solvent displacement reactions can be obtained from the effect of pressure on such processes.[3,4] More recently, Dobson and co-workers have demonstrated the feasibility of studying such reactions in a mixture of solvents of different coordination ability in order to further reveal the nature of the desolvation mechanism.[6,7] Subsequently, we have demonstrated that a combined pressure- and solvent-dependence study can even further assist the elucidation of the intimate solvent displacement mechanism.[8]

In the present investigation we have focused on the solvent displacement reactions of $Cr(CO)_5S$ in a combined pressure- and solvent-dependence study. The results enable an overall comparison of all the available data for this system and allow us to comment on the importance of parallel dissociative and interchange pathways.

Experimental Section

Materials. Details on the solvents and chemicals used in this study are given elsewhere.[7]

Flash Photolysis Studies. These were carried out at the Center for Fast Kinetics Research, Austin, TX, using the flash photolysis system and variable-pressure equipment described previously.[9,10] Further experimental details are similar to those adopted for the ambient-pressure kinetic work.[7] Solutions were flashed in quartz pillbox cells[11] and stirred between experiments with the aid of a small Teflon-coated magnetic stirring bar and a magnetic stirrer placed under the high-pressure cell on the optical rail of the flash photolysis apparatus. The temperature of the high-pressure cell was controlled to within ±0.1 °C with the aid of an external thermostat. The pseudo-first-order rate constants, k_{obs}, were obtained as averages of up to 10 kinetic traces. Limits of error, given in parentheses as the uncertainties of the last digit(s) of the reported values, are 1 standard deviation.

Results and Discussion

In our earlier study of benzene displacement from photogenerated $(\eta^2\text{–}C_6H_6)Cr(CO)_5$ via flash photolysis of $Cr(CO)_6$ in benzene (BZ) solutions,[3] it was suggested that the displacement by piperidine (pip) followed the mechanism outlined in (1).

$$Cr(CO)_5BZ \underset{k_{-1}[BZ]}{\overset{k_1}{\rightleftharpoons}} Cr(CO)_5 \xrightarrow{k_2[L]} Cr(CO)_5L \qquad (1)$$

A variable-pressure study of $Cr(CO)_6$/BZ/pip solutions over a wide range of BZ and pip concentrations,[3] according to the rate law in (2), enabled the determination of the volumes of activation $\Delta V^{\ddagger}(k_1) = +12.3 \pm 1.4$ and $\Delta V^{\ddagger}(k_2) - \Delta V^{\ddagger}(k_{-1}) = -8.3 \pm 1.9$ cm^3 mol^{-1}. The former value is consistent with Cr–BZ bond fission, whereas the latter value indicates less volume collapse during Cr–BZ than during Cr–pip bond formation.

$$k_{obs} = k_1k_2[L]/(k_{-1}[BZ] + k_2[L]) \qquad (2)$$

In a recent ambient-pressure, mixed-solvent study of this system,[7] evidence was presented for parallel dissociative and interchange reaction paths for solvent displacement, depending on the nature of the solvent. This is outlined for fluorobenzene (FB) and *n*-heptane (HEP) as solvents

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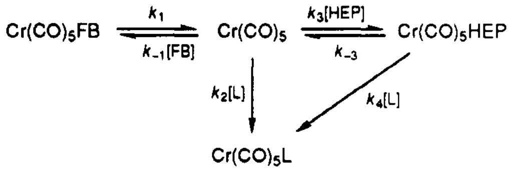
Table I. k_{obs} as a Function of Pressure for the Formation of $Cr(CO)_5pip$ in Various FB/HEP Solvent Mixtures at 25 °C According to the Overall Mechanism Outlined in (3)

[FB], M	[pip], M	[FB]/[pip]	[HEP], M	P, MPa	10^5k_{obs}, s^{-1}	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$
0.887	0.388	2.28	5.99	5	8.73 (19)	9.7 (4)
				50	7.25 (32)	
				100	6.15 (9)	
				150	4.89 (16)	
1.33	0.626	2.13	5.55	0.1	9.44 (4)	9.5 (9)
				50	8.21 (61)	
				150	5.38 (32)	
2.00	0.390	5.12	5.28	5	5.16 (10)	7.5 (1)
				50	4.47 (2)	
				100	3.87 (6)	
				150	3.32 (11)	
2.58	0.300	8.61	4.97	0.1	2.59 (7)	9.6 (10)
				50	1.96 (2)	
				100	1.73 (8)	
				150	1.42 (2)	
4.37	0.376	11.6	3.77	0.1	2.20 (3)	7.9 (5)
				50	1.84 (3)	
				100	1.54 (2)	
				150	1.37 (2)	
5.51	0.399	13.8	2.95	5	1.77 (13)	5.4 (5)
				50	1.56 (2)	
				100	1.46 (4)	
				150	1.273 (5)	
10.1	0.514	19.6	0	0.1	1.375 (7)	6.1 (3)
				50	1.200 (20)	
				100	1.050 (5)	
				150	0.954 (15)	

in (3), with the corresponding rate law in (4). It therefore seemed important to investigate the correlation of $\Delta V^{\ddagger}$ with the nature (nucleophilicity and bonding mode) of the solvent and the suggested mechanism.



(3)

$$k_{obs} = \frac{k_1(k_2 + k_3')}{k_{-1}[FB]/[L] + k_2 + k_3'} \tag{4}$$

$$k_3' = k_3k_4[HEP]/(k_{-3} + k_4[L])$$

The pressure dependence of the $Cr(CO)_6$/FB/HEP/pip system was studied over a wide concentration range of FB and HEP, and the results are summarized in Table I. The observed rate constants decrease with increasing [FB]/[pip], in agreement with the behavior expected on the basis of eq 4.[7] The $\Delta V^{\ddagger}$ values exhibit a specific trend as a function of [FB]/[pip]. As [FB]/[pip] decreases, $\Delta V^{\ddagger}$ increases and reaches an extrapolated maximum of +9.8 ± 0.8 $cm^3\ mol^{-1}$ at [FB]/[pip] $\rightarrow$ 0. According to eq 4 $k_{obsd} \rightarrow k_1$ under these conditions and this value results from the breakage of the Cr–FB bond. It is close to that reported above for the breakage of the Cr–BZ bond, viz. +12.3 ± 1.4 $cm^3\ mol^{-1}$. As [FB]/[pip] increases, $\Delta V^{\ddagger}$ decreases and reaches a low of +6.1 ± 0.3 $cm^3\ mol^{-1}$ in pure FB, i.e. no HEP. Under these conditions eq 4 simplifies to eq 2, and $\Delta V^{\ddagger}$ represents the value for $\Delta V^{\ddagger}(k_1) + \Delta V^{\ddagger}(k_2) - \Delta V^{\ddagger}(k_{-1})$. Once again, this value is in close agreement with that reported above for this reaction in BZ, viz. +4.0 ± 0.5 $cm^3\ mol^{-1}$. Thus, the overall decrease in $\Delta V^{\ddagger}$ as [FB]/[pip] increases can be ascribed to the increasing contribution of $\Delta V^{\ddagger}(k_2) - \Delta V^{\ddagger}(k_{-1})$. It follows that the interchange contribution in the presence of heptane has no significant effect on the value of $\Delta V^{\ddagger}$, which is in line with the general pressure dependence of such processes.[12,13]

Table II. Summary of Available $\Delta V^{\ddagger}$ Data for the Overall Reaction[a]

$$Cr(CO)_5S + L \rightarrow Cr(CO)_5L + S$$

	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$	
solvent (S)	L = hex	L = pip
C_6H_6 (BZ)	+10.9 ± 1.0	+4.2 ± 0.3
$PhCH_3$ (TOL)	+10.8 ± 0.7	+4.8 ± 1.4
PhCl (CB)	+5.4 ± 0.4	+0.2 ± 0.2
PhF (FB)	+9.4 ± 0.7	+6.1 ± 0.3
n-heptane (HEP)	+6.2 ± 0.2	+1.4 ± 0.4

[a] Data not reported in this study are taken from refs 3 and 4.

A comparison of the overall observed $\Delta V^{\ddagger}$ for solvent displacement of $Cr(CO)_5S$ can now be made for piperidine (pip) and 1-hexene (hex) as entering ligands (Table II). According to the general mechanism in (1) the overall $\Delta V^{\ddagger}$ is a composite quantity, viz. $\Delta V^{\ddagger}(k_1) + \Delta V^{\ddagger}(k_2) - \Delta V^{\ddagger}(k_{-1})$. The values of $\Delta V^{\ddagger}$ for S = BZ, TOL, FB and L = hex are so positive that they mainly represent $\Delta V^{\ddagger}(k_1)$ according to the result of this and our earlier study,[3] i.e. $\Delta V^{\ddagger}(k_2) - \Delta V^{\ddagger}(k_{-1}) \approx 0$, or $\Delta V^{\ddagger}(k_2) \approx \Delta V^{\ddagger}(k_{-1})$. This means that the volume collapse during Cr–hex bond formation is similar to that for Cr–S bond formation (S = BZ, TOL, and FB). The values for CB and HEP are significantly smaller; i.e., $\Delta V^{\ddagger}(k_1) - \Delta V^{\ddagger}(k_{-1})$ must be significantly smaller since $\Delta V^{\ddagger}(k_2)$ is expected to be the same as for the other investigated solvents. Exactly the same trend is revealed by the data for L = pip, with the difference that $\Delta V^{\ddagger}$ is on the average 5 $cm^3\ mol^{-1}$ smaller than for L = hex. This can be explained in terms of more effective Cr–pip bond formation, accompanied by a more negative $\Delta V^{\ddagger}(k_2)$ value than for Cr–hex bond formation. Since pip is a significantly stronger nucleophile, we expect more effective overlapping of the molecular radii during bond formation, whereas hex binds more like the solvent molecules FB and BZ, i.e. through an isolated arene double bond.[7] Furthermore, the data in Table II suggest that BZ, TOL, and FB behave very similarly in terms of the associated $\Delta V^{\ddagger}$, independent of the nature of L. The remaining solvents CB and HEP also exhibit a similar behavior, significantly different from that of the other three. This agreement among particular solvents corresponds with the way these molecules coordinate to a metal center:[7] BZ, TOL, and FB are thought to bind via an arene double bond, i.e. in a side-on fashion, whereas CB binds through a lone pair of electrons on the chlorine atom, i.e. in an end-on fashion, and HEP presumably binds in the same way. In this respect it should be noted that F is in general a weak ligand or bridging group compared to Cl, which accounts for the difference in binding modes for FB and CB. Thus, the value of $\Delta V^{\ddagger}(k_1) - \Delta V^{\ddagger}(k_{-1})$, which represents the reaction volume for the dissociation of S from $Cr(CO)_5S$, is significantly larger for the side-on bonding (more effective overlap of molecular spheres) than for the end-on bonding of the solvent. Finally, the significantly more negative $\Delta V^{\ddagger}(k_2)$ value, suggested to account for the less positive overall $\Delta V^{\ddagger}$ values found for the substitution by the stronger nucleophile piperidine, may result from a contribution from a direct attack of pip on $Cr(CO)_5S$, a reaction step not considered in the general scheme (3), but

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not unrealistic to consider. This could result in an interchange (I_d) contribution associated with a less positive ΔV^{*}, as reported for all the reactions with pip in Table II.

The results of this study once again underline the importance of investigating the solvent concentration dependence in an effort to distinguish between various possible solvent displacement mechanisms. This is not always possible, since innocent solvents are not always available to perform such mixed-solvent investigations. In addition, the extended series of ΔV^{*} data now available for solvent displacement reactions of pentacarbonyl complexes enable a more complete comparison and emphasize the important role of the bonding mode of the solvent and its competition with related nucleophiles.

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Registry No. $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5pip$, 15710-39-1; FB, 462-06-6; HEP, 142-82-5; hex, 592-41-6; piperidine, 110-89-4.

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Formation of a Highly-Ordered Polymeric, Supersandwich Metallocene: The First X-ray Crystal Structure of a Base-Free Lithium Cyclopentadienide, $\{[\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4(SiMe_3)]Li\}_n$[1]

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Summary: Crystals of $\{[\mu\text{-}\eta^5:\eta^5\text{-}C_5H_4(SiMe_3)]Li\}_n$ form in the space group $P\bar{1}$ with a = 8.402 (2) Å, b = 11.778 (3) Å, c = 14.740 (4) Å, α = 81.25 (2)°; β = 80.76 (2)°, γ = 77.30 (2)°, V = 1394.1 (5) Å^3, and D_{calcd} = 1.03 g cm^{-3} for Z = 2. Least-squares refinement of the model based on 2902 reflections ($|F_o| > 3.0\sigma|F_o|$) converged to a final R_F = 5.44%. The structure consists of parallel chains of $LiC_5H_4SiMe_3$ units which extend along the b-axis. In each chain, lithium atoms alternate with the $C_5H_4SiMe_3$ rings to form a continuous polymeric sandwich structure. Within a chain, the dihedral angles between cyclopentadienyl planes are 5.1–8.1° and the Li–(ring centroid) distances range from 1.957 to 1.982 Å. The orientation of the $SiMe_3$ substituents in the trimetallic $(LiC_5H_4SiMe_3)_3$ repeat unit found in the chains generates a highly ordered interchain structure.

Introduction

Organolithium complexes hold a prominent position in organometallic chemistry, not only as readily accessible reagents but also as organometallic compounds of the electronically simplest metal.[2] Although organolithium species have been quite attractive for theoretical studies, it has proven to be difficult experimentally to obtain the crystallographic data necessary for optimizing theoretical evaluations. The highly reactive nature of organolithium reagents is compounded by the fact that these complexes tend to oligomerize into noncrystalline materials.

This situation extends even to the cyclopentadienide ligand, which historically has provided so many crystallizable complexes in organometallic chemistry.[3] In recent years, access to crystallographically characterizable lithium cyclopentadienyl complexes has been provided through the use of substituted cyclopentadienides and coordinating bases.[4-14] Table I lists the lithium as well as sodium[9-11] and potassium[10,12,13] structures reported to date. Unfortunately, the extent to which the chelating bases affect the bonding parameters in these compounds is not known since crystal data on the requisite base-free analogs are not available for comparison. Calculations on ammonia adducts of LiC_5H_5 have suggested that there is a significant effect on bonding parameters.[15] The recently reported $\{[C_{24}H_{14}(SiMe_3)_2]Li_2(THF)_2\}_2$[14] has both THF-solvated and

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