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Supplementary Material Available: Tables of X-ray structure determination data for $[Cp^*(Cl)In(\mu\text{-}P(SiMe_3)_2]_2$ and figures showing UV–vis spectra of growing clusters in solution, a transmission electron micrograph, and electron diffraction patterns of In_2O_3 particles and of annealed InP (10 pages). Ordering information is given on any current masthead page.

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Articles

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Concerning the Dependence of the Volume of Activation for a Limiting D Substitution Mechanism on the Size of the Leaving Group. The Aquation of Pentacyano(amine)ferrate(II) Complexes

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A series of limiting dissociative substitution reactions of complexes of the type $Fe(CN)_5(NH_2R)^{3-}$ (R = H, CH_3, C_2H_5, *i*-C_3H_7, and CH_2Ph) were studied as a function of pressure in order to investigate the dependence of the associated volume of activation on the size of the leaving group (NH_2R). The volumes of activation have an average value of +18 $cm^3\ mol^{-1}$ and do not exhibit a meaningful correlation with the size of NH_2R. The results are compared to data available in the literature for other limiting dissociative substitution reactions of octahedral complexes, and a similar conclusion is reached. Possible reasons for this observation are presented.

Introduction

Our group has a longstanding interest in the application of high-pressure techniques in the elucidation of inorganic and organometallic reaction mechanisms.[2-4] It has been one of our goals in the past to find quantitative correlations between the volume of activation (ΔV^{*}) and the partial molar volume ($\bar{V}$) of reactant and product species in terms of a reaction volume profile analysis. With the large quantity of ΔV^{*} data presently available for substitution reactions of octahedral and square-planar complexes in particular, such volume correlations have been useful in the interpretation of the absolute size of ΔV^{*}.[5-12] For instance, in the case of a limiting associative mechanism for square-planar substitution, ΔV^{*} becomes more negative with increasing size of the entering nucleophile due to the more effective overlap of the molecular spheres, as defined by the van der Waals radii.[11,12] In the case of interchange mechanisms (I_a and I_d) for ligand-substitution processes on octahedral metal centers, such correlations are not significant in terms of the size of the entering or leaving groups since only partial bond formation and bond breakage occurs in the transition state. An unanswered question concerns the possibility of such a correlation in the case of limiting dissociative substitution mechanisms.

We therefore studied a series of aquation reactions of octahedral complexes that are known to follow a limiting D mechanism, and for which it was possible to vary the size of the leaving group. For this purpose we selected a series of pentacyano(amine)iron(II) complexes and studied the pressure dependence of their aquation reactions under conditions where iron–amine bond breakage is the rate-determining step.[13-15] The selected amines are NH_3 and NH_2R, where R = methyl, ethyl, isopropyl, and benzyl. The results are discussed in reference to other series of data reported in the literature.

Experimental Section

$Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ was prepared from sodium nitroprusside (Merck, reagent grade) according to standard procedures[13] and characterized by UV–vis spectroscopy and elemental analysis.[16] Pyridine (Janssen), methylamine (Fluka, 25% solution), ethylamine (Raedel de Haen, 50% solution), isopropylamine (Raedel de Haen), and benzylamine (Fluka) were used as supplied. All other chemicals were of analytical reagent grade.

Solutions of $Fe(CN)_5(NH_2R)^{3-}$ (10^{-4} M) were prepared by dissolving $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ in solutions containing 0.02 M NH_2R, 0.01 M HCl, and NaCl (to adjust the ionic strength) and thermostating for 20–25 min. to allow for the complete displacement of NH_3 by NH_2R.[13,14]

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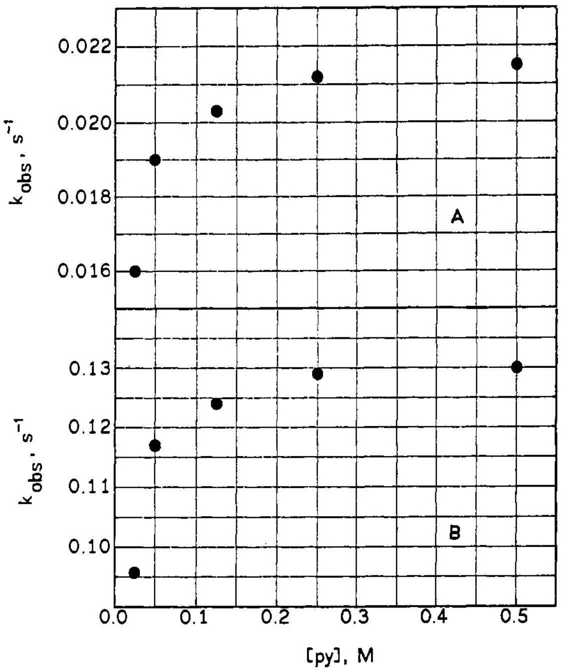

Figure 1. Plots of k_{obs} versus [py] for the reaction $Fe(CN)_5(NH_2R)^{3-} + py \rightarrow Fe(CN)_5(py)^{3-} + NH_2R$. Conditions: $[Fe(CN)_5(NH_2R)^{3-}] = 2.5 \times 10^{-4}$ M; ionic strength = 1.0 M (NaCl); (a) R = H, temperature = 25.0 °C; (b) R = i-C_3H_7, temperature 35.0 °C.

The subsequent substitution reactions were followed on a Durrum D110 stopped-flow instrument at ambient pressure and a homemade high-pressure stopped-flow instrument for pressures up to 100 MPa.[17] For this purpose, the above-prepared solution of $Fe(CN)_5(NH_2R)^{3-}$ was placed in one syringe and a pyridine solution was placed in the other syringe of the stopped-flow instrument. Both instruments were thermostated (±0.1 °C) and attached to an on-line data acquisition system.[18] The substitution reactions were followed at 365 nm where the pyridine complex exhibits a characteristic maximum. First-order behavior was observed for all kinetic runs up to 3 half-lives of the reaction.

Results and Discussion

Various preliminary experiments were performed in order to find the optimal experimental conditions for the studied reactions. In this respect it is essential that solutions of $Fe^{II}(CN)_5(NH_2R)^{3-}$ (R = H, CH_3, C_2H_5, i-C_3H_7, $PhCH_2$) are stable over longer periods of time (ca. 2–3 h) in order to be able to perform the pressure-dependence study in the high-pressure stopped-flow system. For instance the $Fe(CN)_5NH_3^{3-}$ complex rapidly aquates in solution to produce $Fe(CN)_5H_2O^{3-}$, which depending on the concentration and final pH can dimerize to $Fe_2(CN)_{10}^{6-}$, polymerize, or decompose.[13,19,20] In order to avoid this complication, the amine complexes were stabilized by addition of NH_2R/NH_3R^+, typically 0.01 M buffer for a 10^{-4} M complex solution.[13,14] Such solutions were found to be stable and to give reproducible kinetic traces during the overall substitution reaction (1) with

$$Fe(CN)_5(NH_2R)^{3-} + py \rightarrow Fe(CN)_5(py)^{3-} + NH_2R \quad (1)$$

pyridine (py). Another advantage of this system is that both the leaving and entering groups are neutral so that no significant changes in electrostriction are expected to affect the observed activation parameters. The systematic variation of R enables a systematic variation of the size of the leaving group NH_2R.[13,14]

The observed pseudo-first-order rate constant for reaction 1 increases with increasing [py] and reaches a limiting value at high [py] as demonstrated for two typical examples in Figure 1. This finding is in agreement with similar results reported in the literature[13,14] and supports the operation of a limiting D mechanism outlined in (2). The rate law for this mechanism is given in (3),

Table I. k_1 as a Function of Temperature and Pressure for the Substitution of $Fe(CN)_5(NH_2R)^{3-}$ by Pyridine[a]

R	temp, °C	pressure, MPa	k_1,[b] s^{-1}
H[c]	40.0	5	0.110 ± 0.006
		25	0.096 ± 0.001
		50	0.080 ± 0.007
		75	0.071 ± 0.002
		100	0.060 ± 0.004
CH_3[d]	40.0	5	0.026 ± 0.001
		25	0.022 ± 0.0003
		50	0.017 ± 0.001
		75	0.013 ± 0.0005
		100	0.011 ± 0.0005
C_2H_5[e]	40.0	5	0.048 ± 0.001
		25	0.045 ± 0.001
		50	0.040 ± 0.001
		75	0.032 ± 0.001
		100	0.027 ± 0.0003
i-C_3H_7[f]	25.0	0.1	0.037 ± 0.001
	30.0		0.070 ± 0.001
	35.0		0.131 ± 0.002
	40.0		0.193 ± 0.007
	45.0		0.340 ± 0.013
	25.0	5	0.034 ± 0.002
		25	0.030 ± 0.001
		50	0.024 ± 0.001
		75	0.020 ± 0.002
		100	0.017 ± 0.0006
$PhCH_2$[g]	25.0	0.1	0.0060 ± 0.0005
	30.0		0.011 ± 0.001
	35.0		0.024 ± 0.0003
	45.0		0.071 ± 0.002
	40.0	5	0.045 ± 0.001
		25	0.042 ± 0.001
		50	0.036 ± 0.001
		75	0.030 ± 0.001
		100	0.024 ± 0.0005

[a] $[Fe(CN)_5(NH_2R)^{3-}] = 2.5 \times 10^{-4}$ M; [py] = 0.5 M; ionic strength = 1.0 M (NaCl). [b] Mean value of at least five kinetic runs. [c] pH = 9.4. [d] pH = 11.8. [e] pH = 11.9. [f] pH = 11.9. [g] pH = 10.8.

Table II. Rate and Activation Parameters for k_1 for the Overall Reaction $Fe(CN)_5(NH_2R)^{3-} + py \rightarrow Fe(CN)_5(py)^{3-} + NH_2R$

R	k_1 at 25 °C, s^{-1}	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}	ΔV^*, cm^3 mol^{-1}
H	0.0215	102 ± 1[a]	63 ± 5[a]	16.4 ± 0.6[b]
CH_3	0.0028[a]	103 ± 3[a]	54 ± 10[a]	24.0 ± 1.0[b]
C_2H_5	0.0057[a]	104 ± 2[a]	63 ± 8[a]	16.3 ± 1.5[b]
i-C_3H_7	0.037	84 ± 3	9 ± 10	18.5 ± 0.6[c]
$PhCH_2$	0.006	96 ± 3	34 ± 11	17.4 ± 1.4[b]

[a] Reference 14. [b] Temperature = 40.0 °C. [c] Temperature = 25.0 °C.

$$\begin{tikzcd} Fe(CN)_5(NH_2R)^{3-} \arrow[r, shift left, "k_1"] & Fe(CN)_5^{3-} + NH_2R \arrow[l, shift left, "k_{-1}"] \arrow[d, "py"', "k_2"] \\ & Fe(CN)_5(py)^{3-} \end{tikzcd} \quad (2)$$

$$k_{obs} = k_1k_2[py]/\{k_{-1}[NH_2R] + k_2[py]\} \quad (3)$$

from which it follows that $k_{obs} = k_1$ at high [py]. The data in Figure 1 can also be plotted as k_{obs}^{-1} versus $[py]^{-1}$, where k_1 can then be calculated from the intercept (k_1^{-1}) of such plots. For all the investigated reactions there was an excellent agreement between the k_1 values obtained as the limiting k_{obs} at high [py] or as intercepts from the double reciprocal plot procedure described above. The activation parameters for k_1 were therefore measured at a high py concentration, i.e. where $k_{obs} = k_1$, for which the results are summarized in Tables I and II. Under these conditions the studied reactions are also independent of pH.

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Table III. Summary of Available ΔV^* Data for Typical Dissociative Substitution Reactions of Octahedral Metal Complexes

reaction		ΔV^*, $cm^3\ mol^{-1}$	ref
$Fe(CN)_5L^{3-} + CN^- \rightarrow Fe(CN)_6^{4-} + L$			
L = 3,5-Me_2py		$+20.5 \pm 0.8$	22
3-CNpy		$+20.6 \pm 0.5$	22
4-CNpy		$+20.6$	23
2-Mepz		$+19.4$	23
H_2O		$+13.5 \pm 1.5$	24
$Fe^{II}(CN)_5L + X \rightarrow Fe^{II}(CN)_5X + L$			
L = 3,5-Me_2py	X = pz	$+21.2 \pm 1.0$	22
3,5-Me_2py	imH	$+20.3 \pm 1.0$	22
NO_2^-	H_2O	$+20.1 \pm 1.0$	25
NH_3	py	$+16.4 \pm 0.6$	this work
NH_2CH_3	py	$+24.0 \pm 1.0$	this work
$NH_2C_2H_5$	py	$+16.3 \pm 1.5$	this work
$NH_2(i\text{-}C_3H_7)$	py	$+18.5 \pm 0.6$	this work
NH_2CH_2Ph	py	$+17.4 \pm 1.4$	this work
$Co^{III}(NH_3)_4(NH_2)L \rightarrow Co^{III}(NH_3)_4(NH_2) + L$			
L = Me_2SO		$+13.2^a$	9
$OC(Me)N(Me)_2$		$+16.2^a$	9
Cl^-		$+11.0^a$	9
Br^-		$+10.5^a$	9
I^-		$+11.6^a$	9
NO_3^-		$+9.0^a$	9

[a] Calculated for the dissociation reaction of the conjugate-base intermediate after correction for volume changes associated with conjugate base formation (see ref 9).

The data found for k_1 as a function of NH_2R is in good agreement with the available literature data for these and related leaving groups. The associated thermal activation parameters (ΔH^* and ΔS^*) are also in good agreement with those usually found for these type of reactions.[13,14,21] The significantly positive value of ΔS^* is in line with the limiting D nature of the substitution process. The values for ΔV^* are also significantly positive and do not exhibit a specific trend along the series of increasing size of R. The partial molar volumes of NH_2R are 24.8 (R = H), 41.7 (R = CH_3), 58.4 (R = C_2H_5), 85.6 (R = $i\text{-}C_3H_7$) and 109 (R = $PhCH_2$) $cm^3\ mol^{-1}$ at 25 °C, from which it follows that an increase by a factor of 4 does not have a significant effect on the observed ΔV^* for the dissociation of NH_2R. The apparent increase in ΔV^* for NH_3 and NH_2CH_3 may be related to specific interaction with the negatively charged cyano ligands in the latter case during the release of NH_2CH_3.[14] In the case of the bulkier ligands the overall effect is probably controlled by the increased freedom of rotation when NH_2R is released.[14]

The absence of a specific correlation between ΔV^* and the partial molar volume of the leaving ligand in a limiting D mechanism calls for a more detailed discussion. A summary of available ΔV^* data for typical dissociative reactions is given in Table III. The quoted values are all associated with the limiting rate constant for bond breakage. The values for the quoted Fe(II) complexes span a relatively small range especially when the nature and size of the leaving groups are taken into account. The smallest value is reported for the dissociation of a water molecule (viz. +13.5 $cm^3\ mol^{-1}$), which is remarkably close to the limiting value calculated for the dissociation of a water molecule from an octahedral metal center, viz. 13.1 $cm^3\ mol^{-1}$.[26] The values for the larger leaving groups are on the average somewhat larger but do not exhibit a linear correlation with the size of the leaving group. Related data for the dissociation of a ligand on Co(III) complexes, during base hydrolysis via a S_N1CB mechanism, are of a similar magnitude for the dissociation of a neutral ligand and somewhat smaller for the dissociation of an anionic ligand. The latter trend is understandable since charge creation is accompanied by an increase in electrostriction and a decrease in the observed ΔV^*. For instance, the value of +16.2 $cm^3\ mol^{-1}$ calculated for the dissociation of $OC(Me)N(Me)_2$ with a partial molar volume of 90 $cm^3\ mol^{-1}$ is only slightly larger than that expected for the dissociation of a water molecule, viz. 13 $cm^3\ mol^{-1}$ for a partial molar volume of 18 $cm^3\ mol^{-1}$. It follows that, in general, ΔV^* for a limiting D substitution step of octahedral complexes exhibits a minor dependence on the size of the leaving group. This means that the extent of bond breakage in the transition state may vary with the nature of the leaving group to cause an almost constant volume increase. Furthermore, the position of the transition state along the reaction coordinate may vary with the size of the leaving group, and result in an "early" or "late" transition state on a volume basis. In this respect, it is interesting to note that k_1 for the dissociation of NH_2CH_3 is the smallest in the series of complexes studied (Table II) but is accompanied by the largest ΔV^*, i.e. a late transition state. In addition, some reorganization on the remaining five-coordinate intermediate may also partly account for the observed effect, and although this should be constant for a series of similar complexes, it could depend on the location of the transition state as controlled by the leaving group.

The results of this study can also be compared with the ΔV^* data reported for the aquation of $Co(CN)_5X^{3-}$, viz. +7.8 (X = Cl), +7.6 (X = Br), +14.0 (X = I), and +16.8 (X = N_3) $cm^3\ mol^{-1}$ at 40 °C.[27] These data seem to suggest an increase in ΔV^* with increasing partial molar volume of X, which would contradict the findings of the present study if the aquation of $Co(CN)_5X^{3-}$ proceeds according to a limiting D mechanism. Although the authors did interpret these data in terms of a limiting D mechanism,[27] later work by Burnett and co-workers[28,29] demonstrated that an I_d mechanism is more appropriate to account for all the available observations. Furthermore, solvational effects are also expected to contribute toward the quoted numbers since the leaving group is ionic and aquation is accompanied by charge dilution, i.e. a decrease in electrostriction, and complicates their interpretation.

We conclude that there is at most a minor dependence of ΔV^* for limiting dissociative reactions of octahedral complexes on the size of the leaving group. In the case of limiting associative reactions on square-planar complexes, the available data do suggest a more significant dependence on the size of the enetering ligand.[11,12,30] This difference is probably related to the significantly different coordination geometries in both cases.

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