Steric Effects in Ligand Substitution Reactions: Kinetics of the Reaction between Aquo(diethylenetriamine)palladium(II) and Alkyl Sulfides

THOMAS E. JONES,* JACK R. COLE, and BETTY J. NUSSER

The kinetics of the aquo(diethylenetriamine)palladium complex $Pd(dien)OH_2$ reacting with a series of symmetrical dialkyl sulfides have been examined in solvents of 80% methanol/20% water (by weight) and 0.10 M $NaClO_4$ using stopped-flow spectrophotometric techniques. Formation rate constants for the process $Pd(dien)OH_2 + R_2S \xrightarrow{k_f} Pd(dien)SR_2 + H_2O$ have been obtained for R = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, and *tert*-butyl. Second-order rate constants at 25.0 °C for the series methyl, ethyl, *n*-propyl, and *n*-butyl were found to be 1.0×10^4, 4.0×10^3, 2.8×10^3, and 2.2×10^3 $M^{-1} s^{-1}$. Temperature-dependent studies show that ΔH^* is essentially constant, with decreases in k_f due to an increasingly unfavorable ΔS^* term. For the series isopropyl, *sec*-butyl, and *tert*-butyl, second-order rate constants were found to be 3.1×10^2, 1.2×10^2, and 8.2 $M^{-1} s^{-1}$ at 25.0 °C. The decreases in k_f for this series are due primarily to increasing ΔH^* values.

Introduction

Steric effects have long been recognized to be important in metal complexation reactions. The effects of alkyl substitution on the kinetics of complexation reactions of mono- and diamines with first-row transition-metal ions have been extensively examined.[1-5] However, a clear picture of the steric effects on the kinetics of these reactions has failed to appear. This is due, to no small extent, to the complexaties of the amine systems. Because of the basicity of the amines, only a small range of conditions is available where one can have both the aquo metal ion present and sufficient free amine to allow for complex formation. The diamine systems are further complicated by ICB effects.[6] In addition, the amine ligands are highly hydrated.[7] Thus it has been difficult to separate steric effects from other factors contributing to the observed kinetics.

In an attempt to gain some additional insight into the steric effects associated with metal ion complexation reactions, we have examined the kinetics of the reaction between the aquo(diethylenetriamine)palladium(II) complex $Pd(dien)OH_2$[8] and a series of symmetrical dialkyl sulfides. The overall reaction is eq 1. In order to span the widest possible range

$$Pd(dien)OH_2^{2+} + R_2S \rightarrow Pd(dien)SR_2^{2+} + H_2O \quad (1)$$
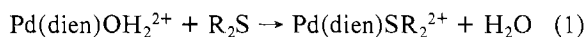
of steric effects, alkyl sulfides included in this study were methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, and *tert*-butyl.

The mechanisms of substitution reactions of d^8 square-planar complexes have been widely studied. Much of this work is summarized in recent reviews.[9-13] The reactions generally proceed through an associative process. The choice of the palladium(II)–alkyl sulfide system for these studies was based on the known affinity of Pd(II) for organic sulfides and the lack of affinity of organic sulfides for protons. In addition the displacement of amines from Pd(II) complexes by organic sulfides has been examined by Cattalini and co-workers.[14]

Experimental Section

Materials. Kinetic studies were carried out in solvents of 80 wt % methanol/20 wt % water (mole fraction of H_2O = 0.30) to circumvent solubility problems with the thia ethers. Absolute methanol (Mallinckrodt) was analytical reagent grade and used without further purification. Deionized water was redistilled using a Corning distillation apparatus. Alkyl sulfides were obtained commercially (Aldrich) and were purified by the following procedure: The sulfides were washed successively with equal volumes of 10% NaOH, 10% HCl, 10% NaOH, and two portions of 10% Na_2SO_4. They were then dried over $MgSO_4$ and distilled. Sulfides with boiling points less than 100 °C were distilled at atmospheric pressure through a 40-cm Vigreaux column. Higher boiling point sulfides were distilled under

a water aspirator vacuum. In each case the constant boiling point, middle fraction was collected and stored in a freezer until use. Sulfide solutions were made up by weight. [Pd(dien)Br]Br and solutions of $[Pd(dien)OH_2](ClO_4)_2$ were prepared by the methods of Basolo and co-workers.[15-17] Sodium perchlorate (G. F. Smith) was recrystallized twice before use. Other chemicals were reagent grade and used without further purification.

Kinetic Studies. Kinetic data were collected utilizing a Durham Model 110 stopped-flow spectrophotometer and a Tektronix Model 549 storage oscilloscope. The temperature was monitored in the water-bath housing on the stopped-flow instrument and was maintained at ±0.1 °C utilizing a Forma Model 2095 water bath. The ionic strength was maintained at 0.10 M utilizing $NaClO_4$. Spectral data on reactants and products were obtained on a Cary 14 spectrophotometer.

All kinetic studies were carried out under pseudo-first-order conditions where the thia ether was always in at least a tenfold excess over the $Pd(dien)OH_2$ complex. Pseudo-first-order rate constants, k_{obsd}, were obtained from plots of $\ln (A_\infty - A_t)$ vs. t. At least six successive kinetics runs were made for each solution. The plots of $\ln (A_\infty - A_t)$ vs. t were linear over the complete reaction, within experimental error, indicating the reaction to be first order in $Pd(dien)OH_2$. The $[Pd(dien)OH_2]$ concentration was varied over the range of $(0.5-20) \times 10^{-5}$ M with no observed variations in k_{obsd}. Reactions at higher palladium concentrations were carried out at the absorption maximum of the 300-nm band for the $Pd(dien)SR_2$ product while the lower palladium concentration studies were carried out at 250 nm which corresponds to the absorption minimum for $Pd(dien)OH_2$ in the UV region. Observed kinetic parameters were independent of the choice of wavelength.

The thia ether concentrations were normally varied over a factor of 50–100. All data were treated assuming a pseudo-first-order reversible system where $k_{obsd} = k_f[R_2S] + k_d$. Thus plots of k_{obsd} vs. $[R_2S]$ would lead to k_f as the slope and k_d as the intercept.

Results

The $[Pd(dien)OH_2]$ complex has an easily displaceable solvent molecule in the inner coordination sphere. The kinetics of the displacement of this water molecule by thia ether donors with varying degrees of alkyl substitution has been examined. The solution spectra of the palladium–thia ether complexes all exhibit intense absorption bands around 300 nm ($\epsilon \sim 10^3$). This band has previously been assigned as a sulfur → palladium charge-transfer band.[18] The $[Pd(dien)SR_2]$ complexes were found to obey Beer's law.

The most probable side reaction to consider would be the opening of one of the nitrogen chelate rings to allow the addition of a second thia ether ligand. This reaction is observed in the reaction of $[Pd(dien)OH_2]$ with macrocyclic tetrathia ethers.[19] The displacement of one of the nitrogen donors is accompanied by dramatic pH increases in the unbuffered reaction mixture. The addition of a second thia ether is not

Table I. Pseudo-First-Order Rate Constants for the Reactions of Dialkyl Sulfides with $Pd(dien)OH_2$[a]

[R_2S], M	t, °C	k_{obsd}, s^{-1}	[R_2S], M	t, °C	k_{obsd}, s^{-1}
		Methyl Sulfide			**n-Butyl Sulfide**
2.06×10^{-2}	25	201, 205	2.56×10^{-2}	25	57.5, 53.4, 54.6, 55.9
1.03×10^{-2}		123, 120, 110, 111	1.28×10^{-2}		28.8, 28.7, 29.1, 29.4, 29.2
6.20×10^{-3}		67.8, 58.5, 65.6, 62.9	6.41×10^{-3}		14.6, 14.7, 16.4, 13.4, 14.1
2.47×10^{-3}		25.9, 25.1, 24.5, 26.3, 24.7, 25.4	5.13×10^{-3}		12.5, 12.0, 11.6, 11.4, 11.4
1.23×10^{-3}		13.7, 12.1, 13.8, 13.6, 14.4	1.03×10^{-3}		2.52, 2.54, 2.72, 2.57, 2.47
4.94×10^{-4}		5.28, 4.90, 5.30, 5.07	5.13×10^{-4}		1.25, 1.21, 1 25, 1.22, 1.18, 1.19, 1.21
4.12×10^{-4}	12.3	2.11, 2.06, 2.13, 2.13, 2.12, 2.16	4.50×10^{-4}		1.12, 1.07, 1.05, 1.27, 1.13, 1.28
4.12×10^{-4}	42.3	6.75, 6.68, 6.81, 6.86, 6.75, 6.86	1.48×10^{-3}	12.3	2.16, 2.09, 2.06, 2.14, 2.10, 2.08
		Ethyl Sulfide	7.42×10^{-3}	42.3	29.5, 29.2, 28.4, 28.9, 28.5, 28.4, 27.7
1.14×10^{-2}	25	45.8, 43.1, 45.7, 44.6, 47.7	1.48×10^{-3}		5.97, 5.85, 5.92, 5.72, 6.03
5.69×10^{-3}		23.7, 24.3, 23.7, 24.2, 23.7			**sec-Butyl Sulfide**
1.42×10^{-3}		6.27, 6.21, 5.76, 6.44	2.87×10^{-2}	25	3.69, 3.45, 3.30, 3.93, 3.69, 3.39
3.55×10^{-4}		1.61, 1.50, 1.48, 1.65, 1.59, 1.61	1.44×10^{-2}		1.90, 2.05, 1.80, 2.01, 1.94, 1.94, 1.90
1.51×10^{-3}	12.3	3.96, 3.88, 4.00, 3.99, 3.78, 4.08	2.87×10^{-3}		0.496, 0.502, 0.507, 0.497, 0.575, 0.593, 0.586
1.51×10^{-3}	42.3	11.2, 11.2, 10.8, 10.3	1.44×10^{-3}		0.294, 0.307, 0.296, 0.317, 0.317, 0.323, 0.293
		n-Propyl Sulfide	2.87×10^{-4}		0.159, 0.153, 0.149
1.97×10^{-2}	25	54.9, 54.4, 57.5, 57.2	2.87×10^{-2}	12.3	1.92, 2.02, 1.97, 2.01, 1.98, 2.04
9.85×10^{-3}		25.7, 27.1, 26.1, 26.6, 25.5, 26.5	2.87×10^{-3}		0.264, 0.261, 0.269, 0.256, 0.253, 0.246, 0.267
3.94×10^{-3}		10.5, 10.5, 11.3, 11.1, 10.7, 10.7	2.87×10^{-2}	42.3	7.77, 8.21, 8.28, 8.21, 7.82, 7.73
9.85×10^{-4}		2.70, 2.58, 2.66, 2.73, 2.58, 2.60	2.87×10^{-3}		1.11, 1.08, 1.03, 1.06
3.94×10^{-4}		1.12, 1.14, 1.19, 1.08, 1.07, 1.04			**$tert$-Butyl Sulfide**
1.97×10^{-4}		0.629, 0.602, 0.606, 0.613, 0.625, 0.584	2.46×10^{-2}	25	0.244, 0.224, 0.233, 0.228
1.18×10^{-3}	12.3	1.97, 1.89, 1.83, 1.94, 1.87, 1.81	1.23×10^{-2}		0.138, 0.134, 0.146, 0.138
1.18×10^{-3}	42.3	5.56, 5.60, 5.48, 5.18, 5.23, 5.29	6.15×10^{-3}		0.0851, 0.0778, 0.0831, 0.0718
		Isopropyl Sulfide	3.08×10^{-3}		0.0544, 0.0600, 0.0597, 0.0543
			1.54×10^{-3}		0.0371, 0.0428, 0.0446, 0.0453
2.55×10^{-2}	25	7.90, 7.77, 7.68, 7.77, 7.46, 8.26, 7.86	6.11×10^{-2}	12.3	0.274, 0.270, 0.266, 0.284, 0.280, 0.269
1.28×10^{-2}		3.44, 3.37, 3.84, 3.29, 3.76, 3.76, 3.47, 3.49	1.52×10^{-2}		0.0847, 0.0832, 0.0800, 0.0818, 0.0832, 0.0800
7.68×10^{-3}		2.34, 2.37, 2.44, 2.16, 2.20	6.11×10^{-2}	42.3	1.17, 1.21, 1.22, 1.17, 1.18, 1.22
2.56×10^{-3}		0.837, 0.845, 0.845, 0.837	1.53×10^{-2}		0.439, 0.435, 0.439, 0.419, 0.439, 0.418, 0.446
1.03×10^{-3}		0.316, 0.328, 0.338	6.11×10^{-3}		0.228, 0.221, 0.237, 0.226, 0.227, 0.226
2.07×10^{-2}	12.3	3.99, 3.81, 3.68, 3.92, 3.71, 3.69			
4.14×10^{-3}		0.833, 0.827, 0.822, 0.868, 0.812, 0.851			
4.14×10^{-3}	42.3	2.82, 2.82, 2.80, 2.77, 2.88, 2.88, 2.78, 2.77			

[a] Rate constants were determined in solvents of 80 wt % CH_3OH/20 wt % H_2O, and 0.10 M $NaClO_4$. $Pd(dien)OH_2$ concentration was varied in the range $(2.0–8.0) \times 10^{-5}$ M.

Table II. Kinetic Parameters for $Pd(dien)OH_2$–Thia Ether Reactions[a]

	k_f, M^{-1} s^{-1}				
R	12.3 °C	25.0 °C	42.3 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
methyl	$(5.14 \pm 0.08) \times 10^3$	$(1.02 \pm 0.02) \times 10^4$	$(1.14 \pm 0.02) \times 10^4$	6.2 ± 0.3	-19.6 ± 0.9
ethyl	$(2.61 \pm 0.06) \times 10^3$	$(3.97 \pm 0.05) \times 10^3$	$(7.21 \pm 0.19) \times 10^3$	5.5 ± 0.1	-23.5 ± 0.3
n-propyl	$(1.60 \pm 0.05) \times 10^3$	$(2.81 \pm 0.02) \times 10^3$	$(4.57 \pm 0.12) \times 10^3$	5.6 ± 0.2	-24.0 ± 0.6
isopropyl	$(1.78 \pm 0.05) \times 10^2$	$(3.05 \pm 0.05) \times 10^2$	$(6.82 \pm 0.11) \times 10^2$	7.6 ± 0.1	-21.5 ± 0.4
n-butyl	$(1.42 \pm 0.03) \times 10^3$	$(2.17 \pm 0.02) \times 10^3$	$(3.90 \pm 0.10) \times 10^3$	5.5 ± 0.1	-24.8 ± 0.2
sec-butyl	$(6.68 \pm 0.05) \times 10^1$	$(1.20 \pm 0.02) \times 10^2$	$(2.68 \pm 0.05) \times 10^2$	7.8 ± 0.1	-22.8 ± 0.4
$tert$-butyl	4.17 ± 0.15	8.24 ± 0.14	$(1.73 \pm 0.03) \times 10^1$	8.2 ± 0.2	-26.9 ± 0.5

[a] Kinetic parameters were resolved from data given in Table I. Uncertainties listed are 1 standard deviation.

observed in the reaction of monothia ether with $Pd(dien)OH_2$ as evidenced by a lack of change of pH upon mixing the reactants. Thus in the reactions reported in this paper the diethylenetriamine chelate remains intact during the reaction. The kinetics were examined in solutions of pH ~4. Variations in pH between 3 and 5 had no effect on observed rates.

Pseudo-first-order rate constants for the different thia ethers are given in Table I. Analysis of this data assuming a pseudo-first-order reversible system leads to the resolved second-order rate constants listed in Table II.[20] Only in the cases of the highly branched alkyl groups are the intercepts significant. The n-alkyl and isopropyl systems go to completion under conditions of the kinetic studies.

In order to evaluate the activation parameter for the series of reactions, the kinetics were examined at three temperatures: 12.3, 25.0, and 42.3 °C. Activation parameters for each system studied were obtained by least-squares fits of the complete data sets to eq 2, where $\ln (k/h) = 23.76$ and $R =$

$$\ln (k_f/T) = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R + \ln (k/h) \quad (2)$$

1.986 cal deg^{-1} mol^{-1}. Activation parameters with their calculated standard deviations are also listed in Table II.

Discussion

Substitution kinetics of $Pd(dien)X$ and $Pt(dien)X$ have been widely examined.[9–12] A two-term rate law of the form rate
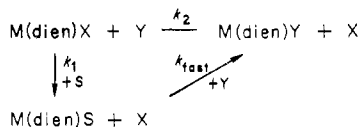
Scheme I

$$M(dien)X + Y \xrightarrow{k_2} M(dien)Y + X$$

$$\downarrow {k_1 \atop +S} \qquad \nearrow^{k_{fast}}_{+Y}$$

$$M(dien)S + X$$

Table III. Exothermodynamic Parameters

R	log k_f at 25 °C	$\Sigma\sigma^{*a}$	$E_s{}^b$	$\Delta\Delta H^{\ddagger}$, kcal/mol	$\Delta\Delta S^{\ddagger}$, eu
methyl	4.01	0.0	0.0	0.0	0.0
ethyl	3.60	0.20	−0.41	−0.7	−3.9
n-propyl	3.45	0.23	−0.56	−0.6	−4.4
isopropyl	2.48	0.38	−1.52	1.4	−1.9
n-butyl	3.34	0.26	−0.67	−0.7	−5.2
sec-butyl	2.08	0.42	−1.93	1.6	−3.2
tert-butyl	0.92	0.60	−3.09	2.0	−7.3

^{a} $-\Sigma\sigma^* =$ sum of Taft inductive effect parameter (ref 21). ^{b} $E_s = $ log (k/k_0), where $k_0 = k_f$ for methyl sulfide.

$= (k_1 + k_2[Y])[M(dien)X]$ is commonly encountered. The two-term rate law is interpreted according to the mechanism of Scheme I. A first-order, Y-independent term is attributed to a pathway involving a solvent displacement of X followed by a rapid displacement of the solvent molecule by Y. The second-order term involves a direct nucleophilic displacement of X by Y. Both pathways involve associative processes.[12]

For the series of studies reported here, Pd(dien)OH$_2$ was chosen as the substrate to eliminate the two-term rate law. Thus we have examined the "fast" displacement of the solvent molecule, water, by the nucleophile Y. Because of the associative nature of these reactions, they are ideally suited for the examination of steric and inductive effects of the incoming ligand. Since bond making is important in forming the activated complex, the observed kinetics should reflect these effects to a maximum extent.

Because of the high affinity of palladium(II) for organic sulfides, it has been possible to examine a much wider range of alkyl groups than has generally been available in the metal amine studies.[2] Thia ethers are protonated only under very highly acidic conditions. In addition, possible effects from the buffer have been eliminated by conducting the study in unbuffered solutions. Thus data interpretation has been greatly simplified as compared to data interpretation of the amine systems.

Inductive Effects. In examining reactions of thia ethers with square-planar palladium(II) complexes it has been common to stress the importance of inductive effects, i.e., the electron-donating or -withdrawing ability of the organic group attached to the sulfur donor atom.[10,14] For sterically unhindered R groups, a linear relationship between log k and $\Sigma\sigma^*$ has been reported in some cases and only qualitative relationships in others, where $\Sigma\sigma^*$ is the sum of the Taft inductive effect parameters.[21] The linear relationships have been interpreted as evidence for the importance of electron-donating R groups in the bond-making process.[10,14]

From the rate constants presented in Table II and from $\Sigma\sigma^*$ parameters for the n-alkyl groups listed in Table III, it is clear that not only is there no linear relationship but the trend in the data is directly opposite that expected from inductive effects. That is, in the case of pure inductive effects, σ^* reflects the observation that the longer the n-alkyl chain, the better electron-donating ability it has. Yet the observed rate constants clearly decrease with increasing chain length. Thus inductive effects are not the dominant factor in the observed kinetics. This does not, however, exclude the possibility of some minor contribution from inductive effects.

The lack of correlation between log k and $\Sigma\sigma^*$ deserves some comment. A relatively small range of $\Sigma\sigma^*$ values was

spanned in this study compared to those studies where linear relationships have been reported.[10] It should also be recognized that the reactions may be mechanistically different. Linear relationships were obtained examining the k_2 pathway while in the current studies the "fast" displacement of the solvent molecule by the sulfur nucleophiles was being examined, i.e., the second step in the solvent pathway. In addition the previous studies were carried out in nonaqueous solvents utilizing an uncharged palladium(II) substrate.

A final possibility is that any observed linear free energy relationship between log k and $\Sigma\sigma^*$ for ligand substitution reactions of square-planar complexes may be fortuitous. The Taft inductive effect parameter is based on the ratios of rates of ester hydrolysis in basic and acidic media. This reaction was chosen to define σ^* because steric interactions at the reaction site should be minimal. This cannot be said for the substitution reactions of thia ethers onto square-planar metal complexes. As can be seen very clearly with molecular models, there is ample opportunity for both interactions between the two R groups attached to the sulfur atom and among the R groups and the ligands already coordinated to the metal ion. Thus linear free energy relationships involving the σ^* parameter should only be expected in cases where steric effects remain constant. The requirement would eliminate n-alkyl sulfides because of the backside interaction between the R groups when the ligand is in a suitable conformation for coordination.

From the above considerations it is concluded that inductive effects are at best only a minor factor in the observed kinetics.

Steric Effects. The variations in k_f as a function of the alkyl substituents on the sulfur donor atom can reasonably be assigned to steric interactions. A number of studies have examined certain aspects of steric effects in square-planar substitution reactions.[10–13,22] It has been shown that highly substituted coordinated ligands retard the substitution rates in accordance with an associative mechanism. Increased alkyl substitution on the incoming ligand has received less attention. However, decreased rate constants with increased branching on the alkyl groups have been noted.[14]

Steric effects in the reactions of n-alkyl-substituted mono- and diamines with first-row transition-metal ions have been more widely studied.[1–6] Rorabacher and co-workers have examined the steric effects for both alkyl-substituted mono- and diamines with Ni(II). They report E_s values for the system studies, where E_s is the Taft steric parameter,[21] defined as E_s = log (k/k_0), in systems where inductive effects are negligible. k_0 is the rate constant for the least sterically hindered member of the series. E_s parameters calculated for the series of alkyl sulfides are listed in Table III. k_0 is taken to be 1.0×10^4 corresponding to k_f for $(CH_3)_2S$. While this approach is qualitatively useful for comparing reactions within a closely related series, it provides little insight into the mechanistic aspects of steric effects on the reaction. For example, there is a poor correlation between E_s values calculated for the same functional group in different reaction systems.[21] Considerably more insight into the mechanistic implications of steric effects can be obtained by a close examination of the activation parameters.

Activation Parameters. Two general observations can be made regarding the activation parameter data shown in Table II. First, large negative $\Delta S^{\ddagger}$ values are observed. This is consistent with an associative process where $\Delta S^{\ddagger}$ reflects the extent of entropy loss during bond making in the formation of the activated complex. This is in general agreement with other reported activation entropies for Pd(II) and Pt(II).[23–25] Secondly, the increased reactivity of Pd(II) complexes over comparable Pt(II) complexes is related to decreased $\Delta H^{\ddagger}$ values for Pd(II). For Pt(II) $\Delta H^{\ddagger}$ values of 20–30 kcal mol^{-1}

are common. The $\Delta H^{\ddagger}$ values of 5–8 kcal mol^{-1} reported here for Pd(II) are within the range of previously reported values.[23,24]

From the data in Table II it can be seen that for the series of *n*-alkyl-substituted sulfides the formation rate constants decrease as the length of the alkyl group increases. From an examination of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values it is clear that there is a trend between increasingly negative $\Delta S^{\ddagger}$ values and decreasing rate constants. The $\Delta H^{\ddagger}$ values are virtually constant within experimental error.[26]

The decreased reactivity of the thiaethers with increasing *n*-alkyl chain length is related to the loss of conformational entropy in forming the activated complex. In order for the electron pairs on the thia ether to interact with the Pd(II) the two alkyl groups must be folded back. Thus when the ligand is in a suitable conformation for coordination, the conformational freedom of the *n*-alkyl groups is greatly restricted. Molecular models suggest that there is considerable interaction between the two alkyl groups.

In the nonlinear alkyl series of isopropyl, *sec*-butyl, and *tert*-butyl, more dramatic differences in the formation rate constants are observed. Here decreases in k_f are paralleled by increasing $\Delta H^{\ddagger}$ values while the trend in $\Delta S^{\ddagger}$ is more irregular. However, it is clear that the $\Delta S^{\ddagger}$ does make a significant contribution. The decreasing reactivity of the thia ethers with increasing alkyl substitution at the α carbons, which is primarily associated with the $\Delta H^{\ddagger}$, can be attributed to increased bond straining due to crowding during the formation of the activated complex. As with the *n*-alkyl thia ethers, the branched alkyl groups must be folded back to expose the sulfur donor atom. Rate retardation effects are associated primarily with the alkyl substituents being forced into the same space. This is clearly an energetically unfavorable situation. There are fewer degrees of conformational freedom available to the branched alkyl groups; consequently $\Delta S^{\ddagger}$ is less important and less conformational freedom is available to be lost in forming the activated complex. *tert*-Butyl sulfide is clearly out of line with the above argument. Its $\Delta S^{\ddagger}$ value is the largest in the series. The *tert*-butyl system undoubtedly represents the maximum possible steric hindrance. Molecular models suggest that the methyl groups in the coordinated *tert*-butyl sulfide would be virtually frozen. This would account for the -4 eu difference in $\Delta S^{\ddagger}$ on going from *sec*-butyl to *tert*-butyl sulfide.

Although generally ignored by coordination chemists, Taft in his classic paper recognized the shortcomings of the steric effect parameter, E_s.[21] In a more detailed examination of the origin of steric effects he concluded that the E_s parameter was a composite term, consisting of contributions from both potential- and kinetic-energy steric effects. The potential-energy term arises from strain energy and is manifested primarily in $\Delta H^{\ddagger}$. The kinetic-energy contribution arises from an increased steric hindrance of motion and is reflected by $\Delta S^{\ddagger}$. The potential- and kinetic-energy contributions can be put on a more quantitative basis by examining $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values for a series of reactions where only an alkyl group has been systematically varied, where $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ are simply the difference between the activation parameters for any member of the series and the activation parameters for a reference R group, usually methyl or hydrogen. The $\Delta\Delta H^{\ddagger}$ value also includes a term for the relative energy of activation associated with inductive effects. Interestingly, the steric strain contribution to the activation enthalpy for aliphatic groups could be correlated between ester hydrolysis reactions and the formation of homomorphic amine–trimethylborane addition compounds even when other linear free-energy and linear steric energy relationships had failed. Of most interest to the current study is the fact that this approach predicts a zero steric strain

contribution to $\Delta\Delta H^{\ddagger}$ for *n*-alkyl functional groups. This is clearly the trend observed in $\Delta H^{\ddagger}$ values listed in Tables II and III. Steric effects in *n*-alkyl groups are reflected entirely in the steric hindrance to motion term (i.e., $\Delta S^{\ddagger}$), again in complete agreement with the data in Table II. This approach has been amplified by others.[27,28]

The difficulties in the application of this approach to ligand substitution reactions are clearly evident. Fairly precise activation parameter data are needed (and are virtually nonexistent). A number of assumptions are inherent in this development; e.g., solvation and resonance effects are assumed to be constant. In spite of these difficulties, this approach seems much more promising than previous attempts in elucidating steric effects on complexation reactions. In fact, the similar qualitative trends in activation parameters, as outlined above, suggest that much of the steric effect data compiled by physical organic chemists may be applicable in metal ion coordination reactions.

Cattallini and co-workers have examined the substitution kinetics for the displacement of amines from Pd(am)$_2$Cl$_2$ species by organic sulfides at 25 °C in dimethoxyethane.[14] Although, as noted earlier, the relative importance of inductive effects appears to differ, there are interesting similarities. In the displacement of substituted pyridines by alkyl sulfides, the ratio of the rate constants for ethyl to isopropyl sulfide is calculated to be 13.1. From the data in Table II that ratio is found to be 13.0. This suggests that the observed steric effects are independent of solvent, leaving group, and charge differences on the Pd(II) substrate.

It is not apparent at this point whether the results obtained in this study can be applied to first-row transition-metal ions since their mechanisms tend to be dissociative. However, from the work of Rorabacher[2] on alkyl amine substitution on Ni$_{aq}$$^{2+}$, it is evident that the qualitative trends in rate constants at 25 °C are the same. Since activation parameters were not determined in that study, it is unclear as to whether there are similar trends in activation parameters. It is obviously an area that deserves more attention.

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Stability of Alkaline Earth Monofluoride Complexes in Methanol

J. W. BIXLER[1] and A. M. BOND*

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Fluoride complexes occupy a central role in ligand-acceptor classification schemes. Depending upon the nature of the acceptor, a given aqueous fluoride complex is either much stronger or much weaker than the other corresponding halide complexes. The extension of these classifications to other solvent systems is made difficult by the dearth of data concerning the stability of nonaqueous fluoride complexes. In this paper, the use of fluoride ion-selective-electrode potentiometry to obtain such data is illustrated with results obtained for alkaline earth monofluorides in methanol and methanol–water mixtures. The weak alkaline earth monofluorides show the stability trend $MgF^+ > CaF^+ > SrF^+ > BaF^+$ in water. The same trend is observed in methanol but the complex stabilities are greatly enhanced compared to the aqueous cases. This enhancement decreases as the atomic number of the alkaline earth increases. The effect of the dielectric constant upon complex stability is illustrated and SrF^+ is shown to obey the Born equation for all water and/or methanol solvent systems, while MgF^+ shows a deviation arising from the strong hydration of Mg^{2+}. Enthalpy and entropy information for MgF^+ and SrF^+ was estimated from temperature variation experiments. The results show that both reactions are entropy-controlled in methanol, as is characteristic for aqueous monofluoride complexes. The variation of the electrode system reference potential as a function of solvent composition is illustrated. Experimental procedure is briefly outlined and difficulties encountered in the nonaqueous measurements using a fluoride ion-selective electrode are described.

Introduction

The schemes developed by Ahrland et al.[2] and Pearson[3] (class a and class b, hard/soft) to systematically classify ligand and acceptor behavior in complexation reactions have proved very useful for making predictions about the stability of various species in aqueous media. However, it is interesting to speculate if these schemes are generally valid in all solvents or are limited to aqueous systems. Ahrland et al. have recently reported some studies of chloride, bromide, iodide, and thiocyanate complexes in the aprotic solvent dimethyl sulfoxide (Me_2SO).[4-8] They report that the class "a" acceptor zinc remains class "a" in Me_2SO, while the "border-line" cadmium ion is class "a" in Me_2SO but class "b" in water. Besides the work of Ahrland and co-workers, little data are available in nonaqueous solvents from which any firm conclusions on the generality of the classification schemes can be made.

The behavior of the fluoride ion, the hardest known ligand, is of major significance in any consideration of the general validity of the classifications. Group "a" acceptors show the halide complex stability trend fluoride $\gg$ chloride $>$ bromide $>$ iodide, while "b" acceptors show the stability trend fluoride $\ll$ chloride $<$ bromide $<$ iodide. Stability constant measurements of fluoride complexes relative to those of the other halides therefore provide a very significant criterion for classifying the metals.

Apart from the direct use in classification studies, another unique feature of fluoride complexes has been noted in aqueous media. Unlike most other systems, there is a strong correlation between the stability of aqueous monofluorides and simple electrostatic interactions arising from the strongly ionic properties of the fluoride ion.[9] Again, no data are available to test this concept as a unifying principle in nonaqueous media. Thus, from at least two important points of view related to systematic classification of stability constants, the paucity of fluoride data in media other than water is unfortunate.

The lack of information regarding the stability of fluoride complexes in nonaqueous media can be attributed to the absence of a simple technique suitable for measuring fluoride activity or concentration in solvents other than water. In particular, the generally low solubility of many metal fluorides in organic solvents means that detection limits must be excellent. In this paper, we report the commencement of our investigation of the stability of fluoride complexes in nonaqueous solvents using a fluoride ion-selective electrode (ISE) to monitor the free ligand concentration.

The utility of ISE potentiometry for the study of complexation equilibria in aqueous solutions is well established.[9-15] The same should be true in other media, although only a few investigations of complex stabilities in nonaqueous systems have been reported.[15] For example, Nakamura and co-workers have reported complex studies undertaken in acetonitrile using cation-sensitive glass electrodes.[16-18] Heerman and Rechnitz have used a cuprous sulfide membrane electrode to study copper(I) complexes in acetonitrile,[19] and Burdin et al. have studied cadmium and zinc chloro complexes in mixed solvents[20] using a chloride ISE. While the fluoride electrode has been used as an end-point detector for titrations in mixed solvents,[21,22] it has only been used as a reference electrode in previous nonaqueous equilibrium studies,[23] and the performance in such media is therefore not well documented. In addition to the intrinsic interest in the stability constant data obtained, the evaluation of the fluoride electrode in nonaqueous solvents also forms an important part of the present communication.

Methanol was chosen as the solvent for this initial investigation for several reasons: Its moderate dielectric constant ($\epsilon = 33$) means that it is a reasonably good ionic medium, while still being significantly different from water in solvent