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Activation Volumes for Hydroxide Attack at Schiff Base Complexes of Iron(II) in Methanol-, *tert*-Butyl Alcohol-, and Dimethyl Sulfoxide–Water Solvent Mixtures[†]

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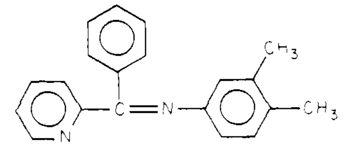
Abstract: The reactions of hydroxide ion with Schiff base complexes [1,8-bis((2-pyridylmethylene)amino)-3,6-diazaoctane]iron(II), where the ligand is hexadentate, and tris[((3,4-dimethylphenyl)imino)phenyl-2-pyridylmethane]iron(II), where each ligand provides two donor nitrogen atoms, have been studied spectrophotometrically. The kinetics of dissociation at several pressures in selected binary aqueous solvent mixtures have been determined at 298 K. At atmospheric pressure the reaction is first order in complex concentration and first order in hydroxide ion concentration in the range ~0.050–0.20 mol dm^{-3}. At higher hydroxide concentrations, particularly with increasing concentration of organic cosolvent, a second-order dependence upon hydroxide ion becomes apparent. Dissociation is accelerated by organic cosolvent (methanol, dimethyl sulfoxide, *tert*-butyl alcohol), slightly more so for the hexadentate complex. This is a reflection of the increase in chemical potential of the hydroxide ion with increasing cosolvent. In water the volume of activation, ΔV^*, is very similar (~+12 cm^3 mol^{-1}) for both complexes, and the sign and magnitude indicate significant loss of electrostricted water. In aqueous methanol, ΔV^* increases dramatically for the tris complex but is markedly reduced for the hexadentate complex. These differences may be attributed to the different preferential solvation of the two complexes, as a consequence of the different nature of their periphery and charge density. The possible effects of the properties of the binary solvents upon the kinetics and activation volumes are also considered.

Kinetics of reactions of low-spin iron(II) complexes of the diimine ligands 2,2′-bipyridyl (bpy) and 1,10-phenanthroline (phen) have been the subject of intensive study for many years.[1] Kinetics of reactions of iron(II) complexes of other diimine ligands, particularly those derived from 2-pyridinecarboxaldehyde or phenyl 2-pyridyl ketone and primary amines, have also been investigated.[2] Despite all these efforts, there still remain several problems relating to mechanism of substitution of these complexes. One problem concerns reactions with hydroxide, cyanide, or alkoxides. Reactions with strong nucleophiles (Nu) of this type follow rate laws of the form[3]

$$-\mathrm{d}[\text{complex}]/\mathrm{d}t = (k_1 + k_2[\mathrm{Nu}])[\text{complex}] \qquad (1)$$

although additional terms may be required in the circumstance of high concentrations of Nu[4] (vide infra). The k_2 term, which is dominant at moderate concentrations of Nu, can be assigned with confidence to a bimolecular process, but whether the initial site of attack is the iron atom or some position in the heteroaromatic ligand is a question of some debate.[5] Another problem is that the activation volumes for attack of hydroxide and of cyanide at $\mathrm{Fe(bpy)_3}^{2+}$ and at $\mathrm{Fe(phen)_3}^{2+}$ are all large and positive (+19.7 to +21.5 cm^3 mol^{-1}).[6] Such values differ dramatically from the value of about −10 cm^3 mol^{-1} expected for a bimolecular process.[7] Subsequent determination of volumes of activation of +4 and −9 cm^3 mol^{-1} for the reaction of the closely related compound $\mathrm{Mo(CO)_4(bpy)}$ with cyanide in methanol and in dimethyl sulfoxide[8] suggests a dominant role for nucleophile desolvation in transition-state formation. However, the large range of ΔV^* values counsels caution in proposing a simple desolvation explanation. In order to gain more information of relevance to these problems, especially the second, we have established activation volumes for reaction of two Schiff base complexes of iron(II) with hydroxide in a selection of binary aqueous solvent mixtures. The Schiff bases were [(3,4-dimethylphenyl)imino]phenyl-2-pyridylmethane (**1**), bidendate, derived from phenyl 2-pyridyl ketone and 3,4-dimethylaniline, and 1,8-bis[(2-pyridylmethylene)amino]-3,6-diazaoctane (**2**), hexadentate, derived from 2-pyridinecarboxaldehyde and triethylenetetramine; their iron(II) complexes will be abbreviated $\mathrm{Fe(sb)_3}^{2+}$ and $\mathrm{Fe(hxsb)}^{2+}$, respectively.



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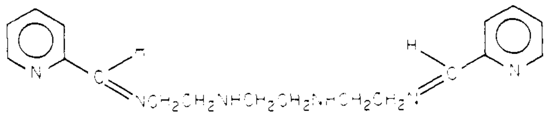

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In this paper we present our results, discuss the key role of solvation, and indicate aspects where further investigation is required before a complete rationalization can be made.

Experimental Section

Materials. [1,8-Bis((2-pyridylmethylene)amino)-3,6-diazaoctane]-iron(II) dichloride and tris [((3,4-dimethylphenyl)imino)phenyl-2-pyridylmethane]iron(II) perchlorate were previously prepared samples.[9] Their characterizations have been reported elsewhere.[10] However, ab-

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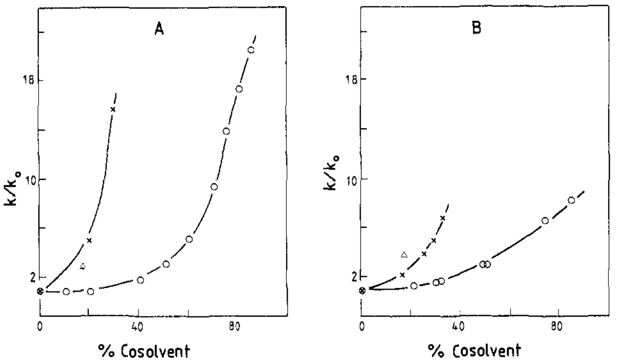

Figure 1. Plots of ratios (k/k_0) of observed first-order rate constants for mixed solvent to those for no cosolvent for dissociation by hydroxide at 298 K [μ = 0.33 mol dm^{-3} (NaCl or KCl)] vs. percent cosolvent (v/v). O = CH_3OH, × = $(CH_3)_2SO$, Δ = t-C_4H_9OH; lines are drawn to illustrate trends and have no theoretical significance. (A) Fe(hxsb)$^{2+}$, [OH$^-$] = 0.33 mol dm^{-3}. (B) Fe(sb)$_3^{2+}$, [OH$^-$] = 0.073 mol dm^{-3}.

sorption spectra were taken to establish that these compounds are stable indefinitely when stored in a darkened desiccator.

Sodium hydroxide, potassium hydroxide, sodium chloride, and potassium chloride were ANALAR grade reagents. Methanol was M and B Pronalys grade or spectrophotometric grade (Aldrich), dimethyl sulfoxide was B.D.H. laboratory grade or spectrophotometric grade (Aldrich), and reagent grade *tert*-butyl alcohol (2-hydroxy-2-methylpropane), a gift from P. P. Duce, was distilled in a Vigreux column before being used. Deionized water was used in making up solutions. Mixed-solvent compositions are by volume, before mixing.

Kinetics. Atmospheric pressure kinetics were determined by using a Unicam SP 8-100 spectrophotometer, a Cary 219 spectrophotometer, or a Unicam SP 1800 spectrophotometer, monitoring the dissociation by hydroxide at 585 and 590 nm for Fe(sb)$_3^{2+}$ and Fe(hxsb)$^{2+}$, respectively, at 298 K. First-order rate plots were linear usually for at least 2–3 half-lives. The kinetics measurement of the loss of absorbance at the cited wavelengths is followed by the formation of a precipitate in the reaction solution; ferric hydroxide and possibly dissociated ligand, particularly at higher volume percentages of methanol and dimethyl sulfoxide, are precipitated. Replicate runs were carried out, and the reported rate constants are average values. Complex concentrations were 8 × 10^{-5} or 1 × 10^{-4} mol dm^{-3} and the hydroxide ion concentration was in the range up to 0.33 mol dm^{-3} for dissociation of both complexes, with the ionic strength made up to 0.33 mol dm^{-3} with sodium chloride or potassium chloride as appropriate.

Kinetics of dissociation at elevated pressures were studied by using the high-pressure apparatus described previously.[11] A typical run involved making up a solution of the appropriate composition, except for dissociating agent, with cosolvent added by suitable volume for the final desired value. Upon reaction initiation by adding aqueous hydroxide solution the reaction solution was divided, with one part being utilized in the high-pressure apparatus and the remaining solution being placed in a cuvette for the atmospheric pressure comparison run. Both solutions were monitored at 298 K; aliquots are withdrawn from the high-pressure system and monitored in the SP 8-100 spectrophotometer. The solvent composition ranges and hydroxide ion concentrations used in high-pressure runs and reported errors in ΔV^* (standard deviations) reflect, in part, practical limitations. In methanol solutions approaching 100% v/v methanol the dissociation of the hexadentate complex is sufficiently rapid that the time-resolution limit of the high-pressure apparatus is reached; this includes both monitoring time and reaction acceleration arising from solution heating upon pressure application. For both complexes this time limit is also approached as the dimethyl sulfoxide component reaches 30–35% v/v. In the mixed aqueous dimethyl sulfoxide solutions insolubility of products and reactants at high pressures also precludes extension of the range of solvent composition. For the dissociation in aqueous dimethyl sulfoxide mixtures, potassium hydroxide and potassium chloride (in the case of Fe(sb)$_3^{2+}$) were used since precipitation problems are reduced in comparison with the sodium compounds. Dissociation at high pressures is reported as the ratio of the observed first-order rate constant at pressure in contrast to the corresponding rate constant at room pressure for the same initial solution. The hydroxide ion concentrations given are those before pressure is applied. *If* the rate constant k_2 of eq 1 were to be used in obtaining ΔV^*, the hydroxide ion concentrations would be increased slightly as pressure is increased resulting in a slightly higher value of ΔV^* for a case of a positive volume of activation. But the difference in value would be well within experimental error. Volumes of activation were calculated from the slope of the plot of the logarithm of the first-order rate constant ratio vs. pressure since these plots showed no systematic deviation from linearity. This implies that the compressibility coefficient of activation, $\Delta\beta^*$, is small and not significant. Therefore, over the pressure range used, 1 atm to 1.35 kbar, ΔV^* is independent of pressure, and the values of ΔV^* recorded are those prevailing for the reaction at room pressure at the solvent composition specified.

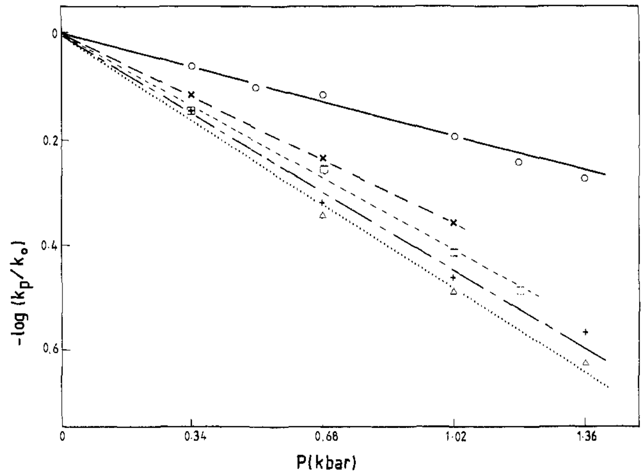

Figure 2. Plot of logarithm of ratio (k_p/k_0) of observed first-order rate constant at pressure, P, to that at atmospheric pressure vs. P for reaction of Fe(sb)$_3^{2+}$ with 0.073 mol dm^{-3} OH$^-$ at 298 K [μ = 0.33 mol dm^{-3} (NaCl)] at various compositions of aqueous methanol. O, — 0%; ×, --- 30%; □, --- 50%; +, — — —, 75%; Δ, ···, 85.3%.

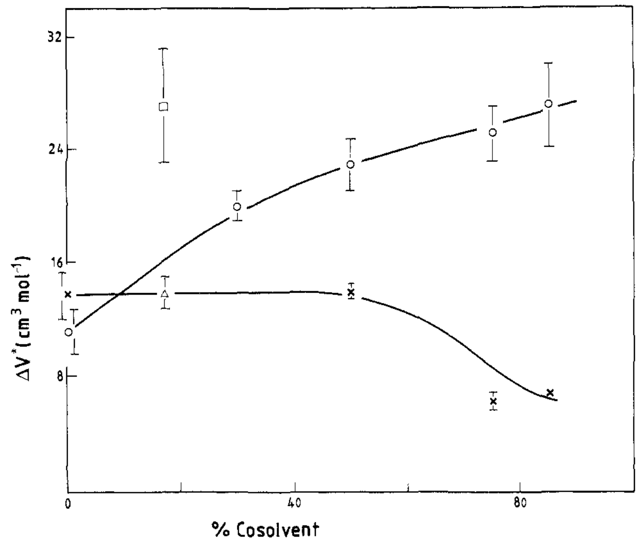

Figure 3. Plot of ΔV^* vs. percent cosolvent (v/v) for dissociation at 298 K by 0.33 mol dm^{-3} OH$^-$ of Fe(hxsb)$^{2+}$, × = CH_3OH, Δ = t-C_4H_9OH, and by 0.073 mol dm^{-3} OH$^-$ (μ = 0.33 mol dm^{-3}) of Fe(sb)$_3^{2+}$, O = CH_3OH, □ = t-C_4H_9OH. Method used in determining ΔV^* indicated in the Experimental Section. Lines are drawn to illustrate trends and have no theoretical significance.

Results

The kinetic results reported in Tables I and II show the variation of observed first-order rate constants with hydroxide concentration and with solvent composition; Figure 1 illustrates the rate enhancements at various cosolvent compositions, compared with dissociation in aqueous solution. Figure 2 contains plots of the logarithm of the rate constant ratio at pressure compared with that at 1 atm (as specified in the Experimental Section) vs. pressure at different aqueous methanol percentages for dissociation of Fe(sb)$_3^{2+}$. The dependence of observed first-order rate constants on pressure at various cosolvent compositions and derived acti-

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Table I. Dissociation of Complexes by Hydroxide Ion at 298 K (μ = 0.33 mol dm^{-3})[a]

$Fe(hxsb)^{2+}$			$Fe(sb)_3^{2+}$		
% CH_3OH, v/v	$[OH^-]$, mol dm^{-3}	$10^5 \times k_{obsd}$, s^{-1}	% CH_3OH, v/v	$[OH^-]$, mol dm^{-3}	$10^5 \times k_{obsd}$, s^{-1}
0[b]	0.050	1.3	0	0.050	4.16
	0.11	2.6		0.073	3.50
	0.17	4.5		0.10	5.14
	0.22	8.0		0.15	7.53
	0.25	9.9		0.20	11.1
	0.28	13.5		0.25	16.5
	0.30	16.0		0.30	25.2
	0.33	20.5		0.33	27.9
0	0.11	0.299	30	0.020	1.32
	0.22	0.689		0.050	3.07
	0.33	1.19		0.073	5.17
30	0.10	0.524		0.10	6.37
	0.15	0.806		0.15	9.50
	0.20	1.05		0.20	12.7
	0.25	1.21		0.25	16.9
	0.30	1.72		0.30	24.0
	0.33	2.00		0.33	26.9
50	0.055	0.623	50	0.020	4.11
	0.11	1.09		0.050	9.27
	0.17	1.74		0.075	12.1
	0.22	2.24		0.10	15.5
	0.26	3.33		0.15	25.5
	0.30	4.09		0.20	32.9
	0.33	4.13		0.26	47.0
75	0.050	1.49		0.33	61.2
	0.11	3.08	75	0.050	17.4
	0.17	5.67		0.075	23.7
	0.22	7.26		0.10	31.7
	0.26	10.8		0.12	44.2
	0.30	13.7		0.15	56.6
	0.33	16.9			
85	0.060	2.25			
	0.080	2.75			
	0.10	3.74			
	0.14	5.85			
	0.18	8.77			
	0.22	10.7			
	0.26	13.1			
	0.30	18.8			
	0.33	23.5			

[a] Rate constants at various $[OH^-]$ and CH_3OH compositions.
[b] 317 K.

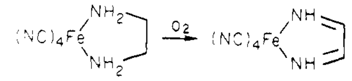
vation volumes are shown in Table III, and plots of ΔV^* vs. percent composition are shown in Figure 3.

The results for the dissociation by hydroxide ion for $Fe(sb)_3^{2+}$ at various solvent compositions (Tables I and II) show that only the second term of the right-hand side of eq 1 is significant at the hydroxide ion concentration used in the high-pressure kinetics studies of this complex; i.e., the reaction is first order in dissociating nucleophile at 0.073 mol dm^{-3} OH^- in all CH_3OH and $(CH_3)_2SO$ compositions studied. In fact the linear dependence of k_{obsd} on hydroxide ion concentration extends to values of ca. 0.20 mol dm^{-3} except at high (75%) methanol concentration.

For practical considerations dissociation of $Fe(hxsb)^{2+}$ at high pressures was studied in most cases at $[OH^-]$ = 0.33 mol dm^{-3}. The kinetic data at atmospheric pressure show that a further term (viz. $k_3[OH^-]^2$) may be manifesting itself at high $[OH^-]$, particularly at high concentrations of organic solvent. At 30% and 50% CH_3OH and 20% $(CH_3)_2SO$ the dependence of k_{obsd} on $[OH^-]$ is essentially linear up to ca. 0.25 mol dm^{-3} $[OH^-]$, and the plots only show relatively slight curvature as $[OH^-]$ is increased to 0.33 mol dm^{-3}. The curvature is more pronounced for the dissociation in 75% and 85% CH_3OH and in 30% $(CH_3)_2SO$. The implication of including additional terms in the rate law for the interpretation of ΔV^* values and comparing or contrasting them with those for dissociation of $Fe(sb)_3^{2+}$ is considered below. However, ΔV^* is independent of hydroxide ion concentration, within experimental error.

Discussion

Before discussing the observed dependences of reactivity on hydroxide concentration, solvent medium, and pressure, it is necessary to consider briefly the structures of the complexes. There is no reason to doubt that the $Fe(sb)_3^{2+}$ cation contains three molecules of **1** acting as bidentate ligands as established previously.[10,12] However subsequent work[13] on related complexes has caused us to investigate the structure of the $Fe(hxsb)^{2+}$ cation. Our original report[14] of the preparation, characterization, and kinetics of cyanide attack of this complex indicated the expected structure of **2**, formed by elimination of water between aldehyde and amine in the normal Schiff base manner, acting as a hexadentate ligand. This structure contains one slightly unusual feature, in that of the six donor nitrogen atoms four belong to diimine moieties, but two are effectively aliphatic amine nitrogens; no low-spin iron(II) complex of the type $Fe(bpy)_2(NH_3)_2^{2+}$ or $Fe(bpy)_2(en)^{2+}$ is known. Goedken[13] has shown that in air the ligand oxidation readily takes place, giving the more strongly coordinating diimine group.



Clearly an analogous oxidation could take place during the preparation of $Fe(hxsb)^{2+}$, to give a hexadentate ligand containing the three diimine groups. Our original characterization did not rule this out;[12] in particular, chemical analysis is unreliable in distinguishing between two possibilities differing only by four hydrogen atoms in such a large molecular weight. We have therefore carried out an X-ray crystal structure determination on $[Fe(hxsb)](NCS)_2$,[15] from which it is clear that ligand oxidation to give a third, central, diimine moiety has not taken place. Bond angles and lengths show unequivocally the presence of the -$NHCH_2CH_2NH$- moiety, as shown in **2**.

The results in Tables I and II illustrate the validity of the rate law (eq 1) at low values of the concentration of attacking nucleophile. For both complexes a higher order dependence on hydroxide ion is apparent, and this is of greater importance at higher values of the organic cosolvent concentration. The rate law would then take the form

$$-d[\text{complex}]/dt = (k_1 + k_2[OH^-] + k_3\,[OH^-]^2)[\text{complex}] \quad (2)$$

and with possibly a term, $k_4[OH^-]^3$, at higher hydroxide ion concentration. It is not pertinent to the discussion here to determine the individual rate constants at each solvent composition since the analysis of the pressure dependence of k_{obsd} is carried out upon results where the higher order term makes a negligible contribution to the rate law or where the pressure dependence of k_{obsd} is independent of concentration of incoming nucleophile.

The rate of reaction at atmospheric pressure increases with an increase in organic solvent; qualitatively the trends are very similar for each complex in each binary solvent under comparable conditions where the reaction is first order in $[OH^-]$. In aqueous methanol rate enhancement is small, up to 40% solvent, but then reaches a factor of 2 to 3 at 50% solvent. Thereafter, the rate increase is significantly larger, reaching a factor of 8 at 85% CH_3OH, the practical cosolvent limit. Similar enhancement values are reached at approximately 20% and 35% in aqueous $(CH_3)_2SO$ solvents. The cosolvent, *tert*-butyl alcohol, at a mole fraction of 0.04 (17%), effects a comparable rate enhancement to ~25% $(CH_3)_2SO$ and ~60% CH_3OH for both complexes. The effect of cosolvent on the rate of dissociation is a reflection of destabilization of reactants relative to the transition state with increase in solvent component. At present it is not possible to dissect the

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Table II. Rate of Dissociation ($10^5 k_{obsd}$, s^{-1}) of Complexes by Hydroxide Ion at 298 K (μ = 0.33 mol dm^{-3})[a]

complex	% $(CH_3)_2SO$, v/v	[OH^-], mol dm^{-3}: 0.050	0.075	0.10	0.15	0.20	0.25	0.28	0.30	0.33
$Fe(hxsb)^{2+}$	20			1.29	1.86	2.71	3.95		5.61	6.58
	30	1.80		3.58	6.07	8.94	11.8	15.4	17.1	20.3
$Fe(sb)_3^{2+}$	17	5.38	8.54	11.5	19.4	27.4	37.2			5.9
	25	8.87	13.7	17.8	28.7	40.0	52.3			63.1
	30	12.3	18.6	25.9	43.8	60.6	75.5			

[a] Rate constants at various [OH^-] and $(CH_3)_2SO$ compositions.

Table III. Ratios (k_p/k_0)[a] of Rate Constants at Pressure P to Those at Atmospheric Pressure for Reaction of Schiff Base Complexes of Iron(II) with Hydroxide in Water and Binary Aqueous Solvent Mixtures and Derived Activation Volumes (ΔV^*) at 298 K

complex	cosolvent	%, v/v	[OH^-],[b] mol dm^{-3}	pressures, kbar: 0.34	0.51	0.68	0.85	1.01	1.18	1.34	ΔV^*, $cm^3\ mol^{-1}$
$Fe(sb)_3^{2+}$	none		0.073	0.88	0.79	0.77		0.63	0.57	0.53	11.1 ± 1.6
	CH_3OH	30.0	0.073	0.77		0.58		0.43			19.9 ± 1.0
		50.0	0.073	0.72		0.55		0.38	0.32		22.8 ± 1.8
		75.0	0.073	0.71		0.48		0.34		0.27	25 ± 2
		85.3	0.073			0.46		0.32		0.24	27 ± 3
		93.8	0.073					0.30		0.21	29
	t-C_4H_9OH	17.0	0.073	0.63		0.42		0.36		0.23	27 ± 4
	$(CH_3)_2SO$	17.0	0.073			0.66	0.58		0.50		15 ± 3
		25.2	0.073	0.76	0.68	0.62					18 ± 3
$Fe(hxsb)^{2+}$	none		0.33	0.76		0.65		0.56		0.49	13.4 ± 1.9
	CH_3OH	50.0	0.33		0.62	0.67		0.58		0.46	14.0
		75.0	0.33	0.93		0.84		0.79		0.70	6.2 ± 0.6
		75.0	0.10				0.83		0.76	0.74	5.5 ± 1.2
		85.0	0.33			0.82		0.76		0.65	6.8
	t-C_4H_9OH	17.0	0.33			0.68		0.55		0.51	14.1 ± 1.1
	$(CH_3)_2SO$	20.0	0.33			0.69				0.47	14
		30.0	0.33	0.74		0.66				0.57	21 ± 3
		30.0	0.10		0.78	0.70		0.59		0.54	11.8 ± 1.6

[a] k_p/k_0 is the ratio (at pressures compared with atmospheric pressure) of observed first-order rate constants at the specified hydroxide ion concentration. [b] The [OH^-] value is that prior to pressure application.

relative destabilization into specific contributions. The chemical potential of the hydroxide ion calculated as the transfer parameter, $\delta_m\mu^\theta$ (OH^-), increases with an increase in cosolvent[16] and parallels the trend of increase in rate constant. Consequently, hydroxide ion dominates among the components possibly subject to destabilization. The relative rate trends for both complexes are fairly similar, suggesting that the complex ions undergo either no solvation or desolvation changes or quite similar changes upon forming the activated complex at each cosolvent mixture. A more detailed examination shows that the dissociation of the larger tris complex is accelerated less under comparable conditions of cosolvent and hydroxide ion concentration; this is compatible with the requirement of the larger structural barrier to $Fe(sb)_3^{2+}$. This difference may contain the key to reconciling the apparent conclusion of significant differences in complex solvation at high cosolvent compositions which emerges from the results of experiments at high pressure.

Reaction in Water. In aqueous solution the volume of activation for each complex is the same within experimental error, a value of +12 $cm^3\ mol^{-1}$. Nucleophilic attack by hydroxide in a bimolecular mode is a reasonable conclusion from the kinetic results; the reaction is first order in concentration of complex and first order in hydroxide ion at low ($\lesssim$0.15 mol dm^{-3}) concentrations. The expected value of ΔV^* for bimolecular reaction based on intrinsic volume changes is about -10 $cm^3\ mol^{-1}$.[7] The difference from the observed value implies a very large solvation effect, on the order of +20 $cm^3\ mol^{-1}$. Upon reaction with the iron complex the hydroxide ion, whether its point of attack is the iron–nitrogen bond or initially at the α position of a pyridyl group, will lose its specific hydration water as it becomes engulfed in the body of the relatively large complex ion. The net positive charge of the resultant species is 1, but this will not give rise to significant electrostriction since the charge, if localized, will be distant from the periphery and, if diffuse, will have a very low charge density, more so in the case of the much larger tris bidentate complex ion. The initial complexes will also be specifically hydrated but to a much lesser degree than the hydroxide ion because of their much lower charge density. The fact that the two complexes give rise to essentially the same ΔV^* in water argues against their contributing significantly to the solvation component of ΔV^* or contributing to a similar but small extent. Both the initial and transition-state configurations of each complex ion will have different hydration because of the difference in size and detailed structure. With the assumptions that release of electrostricted water from the hydroxide ion is the dominant contribution to the solvation component of ΔV^* and that this release is comparable for reaction at both complex ions, independent of detailed mode of hydroxide attack, the transition state is reached with the accompanying transfer to bulk solvent of six or seven electrostricted water molecules per reacting pair. This estimate can be made since transfer per molecule of water is thought to be about 3 cm^3 mol^{-1}.[17]

Reaction in Aqueous Methanol. The changes in ΔV^* with increasing amount of CH_3OH are strikingly different for the two complexes (Table III and Figure 3); for $Fe(hxsb)^{2+}$ ΔV^* is approximately halved at 75% CH_3OH from its value in water, whereas dissociation by hydroxide of $Fe(sb)_3^{2+}$ is accompanied by a doubling of ΔV^* when 75% solvent water is replaced by methanol. The initial assumptions that would be made are that desolvation of hydroxide, changes in solvent bulk properties such as the breakdown of water structure by a typically aqueous (TA) cosolvent[18] such as methanol, and changes in the effective molar volume of water are identical for both reacting systems when a common binary solvent is considered. It is further assumed that

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the hydroxide ion is preferentially hydrated in all aqueous methanol solutions used. However, the mechanism of dehydration of hydroxide ion may be different as the nucleophile approaches the respective ions. The $Fe(hxsb)^{2+}$ species has a large degree of its periphery occupied by aliphatic groups, and in aqueous methanol mixtures the two secondary and two tertiary aliphatic nitrogen atoms may participate in hydrogen bonding with water molecules. The two 2-pyridyl residues would favor solvation by the methyl group of methanol rather than water or the hydroxy moiety of methanol, although this may be of small significance when the central ion has a positive charge of 2. An approach of the hydrated hydroxide ion to its final point of attack at either possible site would be facilitated, presumably, by passing through the water-like surrounding of the complex ion in its aliphatic portion rather than hindered by a pathway through a methanol-rich hydrophobic region. Upon reaction the net charge of the complex is reduced by one unit. Therefore, the water of hydration of the complex ion, to now somewhat electrostricted, would then be partly released. It is not possible to be definite about the extent of release when bulk solvent has a higher percent of methanol. A smaller volume of the complex ion from this contribution is a consequence when the water structure is not maintained. In the other region of the complex ion the methanol solvation would be expected to be increased due to the charge reduction as reaction occurs. It could be argued that this causes an increase in volume, or it could be considered that the stronger hydrophobic bonding indicates more tightly held methanol and thus a smaller volume. A combination of these factors is probably responsible for the reduction in ΔV^* from +13 to +6 $cm^3\ mol^{-1}$ as CH_3OH is increased from 0% to 75%.

Dissociation of $Fe(sb)_3^{2+}$ is accompanied by an increase of ΔV^* from +11 to +27 $cm^3\ mol^{-1}$ as the aqueous solvent is changed to 85% CH_3OH. The complex ion is very much larger and contains nine aromatic residues. There is virtually no opportunity for hydrogen bonding with the ligand and specific hydration is only by virtue of the charge upon the ion. The latter effect would be expected to cause only weakly electrostricted solvent since the charge density is very low compared with $Fe(hxsb)^{2+}$. In aqueous methanol mixtures the nature of the complex ion solvation should be reasonably uniform around the periphery of this ion in contrast to solvation of $Fe(hxsb)^{2+}$. Solvation by the methyl groups of methanol due to the hydrophobic attractions with the ligand may be anticipated; however, it is not certain that the influence of charge cannot maintain some hydration and solvation by the hydroxy moiety of methanol. The incoming nucleophile approaches through a similar solvation medium whichever direction it takes, and orientation of the reaction pair is less specific than it is for reaction of $Fe(hxsb)^{2+}$ because of this and because there are three possible sites of attack within the complex ion. When the hydroxide ion loses its hydrating water molecules to the solvent is not clear, but it probably happens in consecutive fashion as the nucleophile penetrates the network of the solvating molecules of the ligand en route to the bond breaking location. Upon reaction, the net charge is reduced and the large increase in volume of the activated complex over that in aqueous medium could be due to a significant increase in solvation by methanol, an effect that has larger magnitude as the methanol cosolvent increases.

Reaction in Other Solvents. *tert*-Butyl alcohol, also a TA solvent,[18] effects a change in water structure at a mole fraction of 0.04 (~17% v/v).[19] The fact that at this composition ΔV^* for the dissociation of $Fe(sb)_3^{3+}$ is +27 $cm^3\ mol^{-1}$ and this value parallels those at 75% and 85% methanol (+25 and +27 $cm^3\ mol^{-1}$) is indicative of the importance of this change in water structure and the subsequent possibility of solvation influence of the complex ion both in initial state and transition state by the organic moiety of the alcohol. This aspect of *tert*-butyl alcohol influence upon water does not appear to be as important in the dissociation of $Fe(hxsb)^{2+}$ since ΔV^* is the same within experimental error for 100% H_2O, 50% CH_3OH, and 17% $t\text{-}C_4H_9OH$ (Table III).

The effect of a typically nonaqueous negative (TNAN) solvent, dimethyl sulfoxide,[20] upon ΔV^* is more difficult to interpret from the limited data available (Table III). A similar trend as for the reaction in CH_3OH is observed in that ΔV^* increases with increasing amount of cosolvent, but with smaller magnitude increases, scarcely beyond experiental error, for dissociation of $Fe(sb)_3^{2+}$. Dissociation of the hexadentate complex in aqueous $(CH_3)_2SO$ yields ΔV^* values which suggest the volume of activation may depend upon hydroxide concentration or the differences for a common percent of $(CH_3)_2SO$ may reflect the participation of a second hydroxide in the dissociation at high hydroxide concentration, as anticipated from eq 2. This point may be worthy of further investigation; however, in aqueous CH_3OH the indication is that ΔV^* is not influenced by the concentration of attacking nucleophile.

Conclusion

The reactions studied are associative in character, and yield, in water, very similar ΔV^* values indicative of signifciant loss of electrostricted water. In binary aqueous solvent mixtures the dissociation is not accompanied by parallel trends in ΔV^* for the two complexes. These results show that solvation both of hydroxide and of the iron(II) complexes must play an important role in determining the observed reactivity trends as pressure and solvent composition are varied. The next step in the elucidation of this key role of solvation effects is the establishment of transfer chemical potentials for the two iron(II) complex cations from water into various binary aqueous solvent mixtures. This will involve not only measurements of solubilities of selected sparingly soluble salts of these cations but also considerable efforts to reconcile the different assumptions used in deriving the currently available sets of single ion transfer chemical potentials in the three sets of solvent mixtures used in the present paper.

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Registry No. $Fe(Sb)_3^{2+}$, 20149-75-1; $Fe(hxsb)^{2+}$, 88686-51-5; OH^-, 14280-30-9; CH_3OH, 67-56-1; Me_2SO, 67-68-5; $t\text{-}C_4H_9OH$, 75-65-0.

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