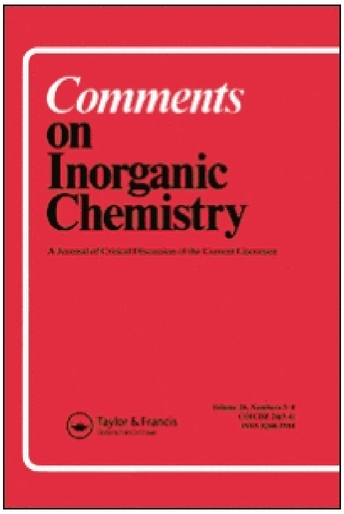

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Activation Volumes and Their Variation with Solvent Composition for Dissociation of Iron(II)—Diimine Complexes in Acidic and Basic Media

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Activation Volumes and Their Variation with Solvent Composition for Dissociation of Iron(II)–Diimine Complexes in Acidic and Basic Media

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A summary of published work on the kinetics of dissociation of iron(II)–diimine complexes in aqueous or aqueous solvent mixtures in the presence of acid or base is presented. There is an emphasis on the use of the volume of activation as a means of addressing questions of mechanism and solvation. This account indicates that available results can be interpreted to show that dissociation proceeds by an associative mode of activation in a basic medium and by a dissociative path in acidic solution.

Key Words: *iron(II)–diimine complexes, high pressure kinetics, volumes of activation, substitution mechanisms*

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INTRODUCTION

Kinetics of substitution of low-spin iron(II) complexes of diimine ligands of the 2,2′-bipyridyl (bpy) and 1,10-phenanthroline (phen) type have been studied for many years, since the original experiments of Baxendale and George.[1] The specific reaction of dissociation in the presence of particular nucleophiles (hydroxide or cyanide attack) has been the subject of much attention since Margerum and Morgenthaler's establishment of the rate laws for the $Fe(phen)_3^{2+}$ cation in 1962.[2] The dominant pathway, especially in water and in water-rich binary solvent mixtures, is a second order term, $k_2[\text{complex}][OH^-]$, or comparably, $k_2[\text{complex}][CN^-]$. This is the case for a large number of complexes of this type. There has been considerable controversy,[3] still unresolved,[4] as to whether these rate law terms refer to hydroxide or cyanide attack at the iron or at some point on the coordinated diimine ligand. The progress of this debate can be followed through regular periodical reports.[5] Although this question is obviously of fundamental mechanistic importance, it is only of relatively marginal significance in the present context, since the following discussion applies in equal measure to either route, being primarily concerned with the bringing together of two separate solvated species to form a single entity, the molecular configuration of the transition state. However, some cases in which a nucleophile appears to attack the ligand first will be discussed.

Medium effects on reactivity have been extensively studied for dissociation, racemization, and base hydrolysis of these iron(II)–diimine complexes.[6] Reactivity trends for well-documented substitution reactions are invaluable for probing medium and solvation effects in ranges of single and mixed solvents and in "organized media" such as micelles, vesicles, and microemulsions.[7] Such studies on these iron(II) complexes date back to those of dissociation of $Fe(phen)_3^{2+}$ in methanol–water mixtures,[8] since when numerous other studies of racemization, dissociation, and base hydrolysis have been published, analyzed, and discussed.[9] Hydroxide attack has proved popular, since changing solvation of the two reactants and of the transition state can be tracked through rate constant trends and their dissection into initial state and transition state components. Hydroxide attack has also been examined in several micellar and microemulsion systems, since the hydrophilic hydroxide and hydrophobic complex, with their different solvation environment requirements, provide useful monitors of the nature of reaction sites.[7] In certain cases these requirements cause not just a change of reactivity but a change in rate law.[10]

Most investigations of medium effects on reactivity deal with reactivity trends in terms of rate constants (k or ΔG^*), and a reasonable number of enthalpy and entropy of activation parameters (ΔH^*, ΔS^*).[11] Recently it has begun to be appreciated that pressure effects on reactivity, reflected in activation volumes, (ΔV^*), can also provide valuable information on solvation effects in reactions of a well-established mechanism.[12] Indeed this approach is usefully complementary to initial state–transition state analysis. This latter analysis is informative for changes of solvation of the two states, respectively, on transfer between solvent media, while activation volumes provide information on solvation changes on going from the initial state to the transition state in individual media (cf. Fig. 1). Dissociation of and nucleophilic attack by hydroxide at iron (II)–diimine complexes are, in principle, attractive reactions to use in the probing of solvation effects by these

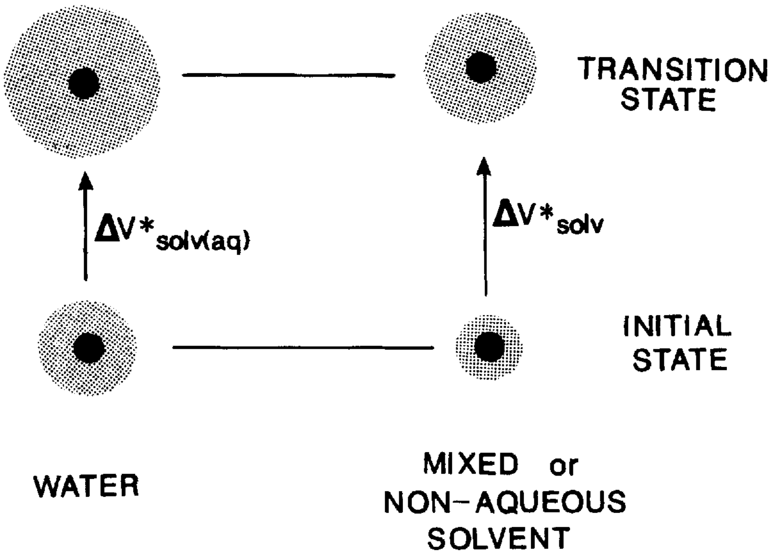


FIGURE 1 Schematic of initial state and transition state species in two different media.

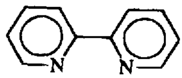
complementary approaches. Indeed we have been following this route with a measure of success for a while.[13] Nonetheless there are several significant problems in relation both to ligand effects on activation volume in aqueous solution and to solvent effects on activation volumes in series of binary aqueous media. It is the purpose of this article to review these problems, to enumerate them, to indicate the present position, to suggest what might be done to resolve them, and to outline the current state of understanding of solvent effects in these systems.

ACTIVATION VOLUMES: AQUEOUS SOLUTION

We will start with the sign and magnitude of ΔV^* in aqueous solution, and how these are affected by the nature of the diimine ligand; the various diimine ligands, bi-, ter-, and hexa-dentate, referred to in this article, are depicted, with their respective abbreviations, in Scheme 1. Values of ΔV^*, for aquation and for hydroxide or cyanide attack, are collected together in Table I. For aquation, ΔV^* values are positive, consistent with the expected dissociative mechanism, and cover the range +11 to +22 $cm^3\ mol^{-1}$.[14] They are ligand dependent, but ΔV^* does not correlate with volumes of the leaving groups and, indeed, while only limited data are available, varies with the reagent, allowing aquation to occur.[14] In the former case this has been attributed to mark-

1	bipy	
2	phen	
3	$X = Y = CH_3$	Me_2bsb
4	$X = CH_3, Y = H$	3Mebsb
5	$X = H, Y = CH_3O$	4MeObsb
6	hxsb	
7	gmi	
8	$R = CH_3$	PMI
9	$R = C_2H_5$	PEI
10	$R = n - C_3H_7$	PPI
11	$R = n - C_4H_9$	PBI
12	Me_2tsb	
13	ppsa	
14	$X = SQ_3^-$	fer
15	$X = H$	fertri

SCHEME 1 Formula and structure of ligands.



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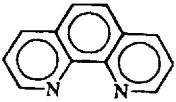

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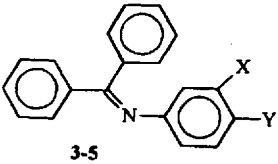

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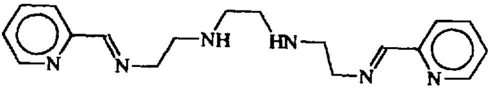

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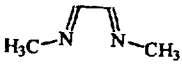

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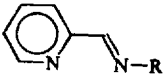

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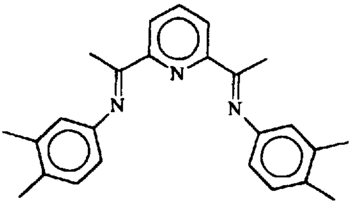

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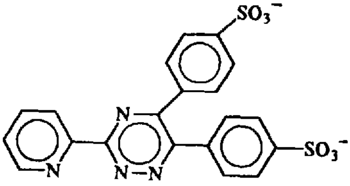

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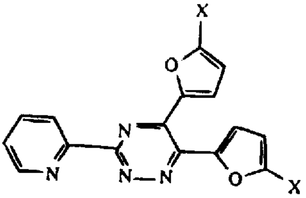

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TABLE I

Activation volumes for dissociation of iron(II)–diimine cations in aqueous solutions.

Complex[a]	Reactant	I (mol dm^{-3})	ΔV^* (cm^3 mol^{-1})	T(K)	Ref.
$[\mathrm{Fe(bpy)_3}]^{2+}$	NaCN	0.10	20.9 ± 1.6	293.2	15
	NaOH	0.10	21.5 ± 0.4	293.2	15
	NaOH	0.010	12.8 ± 0.4	298.2	14(b)
	KCN[b]	0.33	12.2 ± 1.5	298.2	17
$[\mathrm{Fe(phen)_3}]^{2+}$	NaCN	0.10	19.8 ± 1.0	293.2	15
	NaOH	0.10	19.7 ± 0.3	293.2	15
	NaOH	0.0050	14.2 ± 0.8	298.2	14(b)
	KCN[b]	0.33	10.5 ± 1.5	298.2	17
$[\mathrm{Fe(4,4'\text{-}Me_2bpy)_3}]^{2+}$	KCN[b]	0.33	12.3 ± 1.5	298.2	17
	NaOH	0.010	11.7 ± 1.5	298.2	17
$[\mathrm{Fe(4\text{-}Mephen)_3}]^{2+}$	KCN	0.033	10 ± 2	298.2	13(a)
$[\mathrm{Fe(Me_2bsb)_3}]^{2+}$	KOH[c]	0.33	11.1 ± 1.6	298.2	13(b)
$[\mathrm{Fe(3Mebsb)_3}]^{2+}$	KOH[c]	0.33	13.6 ± 1.8	298.2	14(b)
$[\mathrm{Fe(4MeObsb)_3}]^{2+}$	KOH[c]	0.33	12.0 ± 2.1	298.2	14(b)
$[\mathrm{Fe(hxsb)}]^{2+}$	NaOH[d]	0.33	13.4 ± 1.9	298.2	13(b)
$[\mathrm{Fe(gmi)_3}]^{2+}$	NaOH[d]	0.33	16.7	298.2	14(b),16
$[\mathrm{Fe(5\text{-}Brphen)_3}]^{2+}$	EDTA	0.030	22.3 ± 1.0	298.2	14(b)
$[\mathrm{Fe(5\text{-}NO_2phen)_3}]^{2+}$	EDTA	0.030	21.7 ± 1.0	298.2	14(b)
$[\mathrm{Fe(5\text{-}NO_2phen)_3}]^{2+}$	H_2SO_4	3.0	17.9 ± 0.3	308.2	14(a)
$[\mathrm{Fe(phen)_3}]^{2+}$	H_2SO_4	3.0	15.4 ± 0.4	308.2	14(a)
$[\mathrm{Fe(4,7\text{-}Me_2phen)_3}]^{2+}$	H_2SO_4	3.0	11.6 ± 0.6	308.2	14(a)
$[\mathrm{Fe(bpy)_3}]^{2+}$	HCl	1.0	12.3 ± 0.5	303.2	14(d)
$[\mathrm{Fe(bpy)_3}]^{2+}$	HCl	0.01	14.8 ± 0.7	308.2	14(d)
$[\mathrm{Fe(4,4'\text{-}Me_2bpy)_3}]^{2+}$	HCl	1.0	12.5 ± 0.7	298.2	14(e)
$[\mathrm{Fe(4,4'\text{-}Me_2bpy)_3}]^{2+}$	HCl	0.01	15.5 ± 0.5	298.2	14(e)
$[\mathrm{Fe(4,4'\text{-}Et_2bpy)_3}]^{2+}$	HCl	1.0	12.7 ± 0.6	298.2	14(e)
$[\mathrm{Fe(4,4'\text{-}Et_2bpy)_3}]^{2+}$	HCl	0.01	16.9 ± 0.6	298.2	14(e)
$[\mathrm{Fe(5,5'\text{-}Me_2bpy)_3}]^{2+}$	HCl	1.0	13.7 ± 0.5	298.2	14(e)
$[\mathrm{Fe(5,5'\text{-}Me_2bpy)_3}]^{2+}$	HCl	0.01	17.4 ± 0.8	298.2	14(e)
$[\mathrm{Fe(phen)_3}]^{2+}$	CF_3SO_3H (100% CH_3OH)	0.1	14.1 ± 0.2	310.0	14(e)
$[\mathrm{Fe(TMI)_3}]^{2+}$	HCl	2.0[e]	11.5 ± 0.03	316.2	14(c)
$[\mathrm{Fe(PEI)_3}]^{2+}$	HCl	2.0[e]	14.2 ± 0.03	313.2	14(c)
$[\mathrm{Fe(PPI)_3}]^{2+}$	HCl	2.0[e]	13.0 ± 0.03	308.2	14(c)
$[\mathrm{Fe(PBI)_3}]^{2+}$	HCl	2.0[e]	13.1 ± 0.03	308.2	14(c)
$[\mathrm{Fe(Me_2tsb)_2}]^{2+}$	NaOH	0.33	6	298.2	32

[a] Ligands and abbreviations are defined in the text and in Scheme 1.

[b] 0.010 mol dm^{-3} KCN, and NaCl was used to maintain ionic strength.

[c] KCl was used to maintain the ionic strength.

[d] NaCl was used to maintain the ionic strength.

[e] 2.0 mol dm^{-3} made up of 0.100 mol dm^{-3} HCl and 1.900 mol dm^{-3} LiCl.

edly different extensions of the iron–nitrogen bonds in forming the transition state, which of course depends on bond strengths, not on ligand volumes. To account for the difference in ΔV^* for the same ligand dissociating, the difference in ionic strengths of the aquation media has been proposed as an explanation.[14b] However, more results would be needed to examine this aspect; yet at the same time there are few suitable ligands for this purpose. It has been suggested that a major fraction of the measured positive ΔV^* values for aqueous $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$, and by logical extension the argument would apply to other low spin iron(II)–diimine complexes, can be ascribed to a low spin $\rightleftarrows$ high spin preequilibrium of the iron(II) species. The remaining volume change, only about 1 $cm^3\ mol^{-1}$, would result from the dissociative mode of activation, according to this scheme.

Turning to nucleophilic attack in aqueous solution, reported ΔV^* values range from $+10$ to $+22$ $cm^3\ mol^{-1}$ with both attack by hydroxide and cyanide falling within that range.[15–17] The initial high pressure measurements[15] were for dissociation of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ in the presence of either OH^- or CN^-; all values of ΔV^* were in the $+20$ and $+22$ $cm^3\ mol^{-1}$ range which prompted these authors to invoke a dissociative mechanism in spite of contrary evidence from the rate law[2] in the case of $Fe(phen)_3^{2+}$. Other authors have supported the dissociative mechanism for base hydrolysis, although no addition experimental evidence was presented.[18]

While still obtaining distinctly positive values (Table I), we have not obtained exactly the same values of ΔV^* for nucleophilic attack as those reported earlier. The parameters were obtained under slightly different conditions, and due allowance for error associated with acquiring both sets of kinetic data can be given; but even then there is an unexplained discrepancy between the ΔV^* values. However, all other iron(II)–diimine complexes yield values of ΔV^* for reaction of hydroxide in the $+10$ to $+16$ $cm^3\ mol^{-1}$ range. We interpret these values, all distinctly positive in contrast to a value of about -10 $cm^3\ mol^{-1}$ for bimolecular processes in the absence of solvent, as suggesting that solvation plays a dominant role. Qualitatively, these positive values can be ascribed to extensive desolvation of the incoming nucleophile on entering the transition state. This can hardly be the sole explanation, since this would indicate a desolvation contribution of between 20 and 30 $cm^3\ mol^{-1}$, which seems an excessively large amount. The difference in volume between a bulk water molecule and one subject to electrostriction by a 2+ ion such as Fe^{2+} has been estimated to be 2–3 $cm^3\ mol^{-1}$.[19] In addition it would be surprising if desolvation of a hydroxide ion and a cyanide ion made equal contributions, as would be required to explain the near equality for ΔV^* values for OH^- and CN^- attack at the $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ cations, since the partial molar volumes $\bar{V}$ of these two anions differ considerably [$\bar{V}(CN^-) = +24\ cm^3\ mol^{-1}$ and $\bar{V}(OH^-) = -4\ cm^3\ mol^{-1}$].[20,21] We have begun to find other examples where $\Delta V^*\ (OH^-) \simeq \Delta V^*(CN^-)$, although more examples are needed, and work is in progress in this connection. Calculations of intrinsic and solvational contributions of $\bar{V}$ values are planned with a view to quantifying these features.[22] It would also be useful to have some pairs of $\Delta V^*(OH^-)$ and $\Delta V^*(CN^-)$ values for other diimine complexes, to test the generality of $\Delta V^*(OH^-) \simeq \Delta V^*(CN^-)$; such studies are also in progress. It should, of course, be borne in mind that in an S_N2 reaction there is bond extension to the leaving group as well as bond formation to the incoming group. The relatively large volumes of these diimine leaving groups suggests that this should contribute significantly to the overall observed ΔV^* values. The limit of such contributions is set by ΔV^* (dissociation) values, which are in the range +12 to +20 $cm^3\ mol^{-1}$ (cf. above). The actual contribution to ΔV^* (S_N2) would be much less than for these aquation ΔV^* values, but could easily convert the gas phase value of $-10\ cm^3\ mol^{-1}$ to around zero. As for aquation, ΔV^* values do not correlate at all with ligand volumes, or even with estimated cross-sectional areas perpendicular to the direction of leaving.[23] Additional support for the mechanistic distinction between aquation (dissociative) and nucleophilic attack (associative) comes from enthalpies and entropies of activation.[14b] For base hydrolysis, ΔH^* is typically about 90 kJ mol^{-1} and for aquation is close to 120 kJ mol^{-1}. Aquation is accompanied by ΔS^* values of about 80 J $mol^{-1}\ K^{-1}$, while these parameters, yet still positive, are of much smaller magnitudes for nucleophilic dissociation (OH^-).

There is a general correlation between bond length, bond strength, and reactivity with respect to aquation or hydroxide or cyanide attack for many iron(II) complexes, and for an example where there is not, the explanation may reside in a different combination of σ/π bonding characteristics.[14a] As indicated earlier, although there are few examples, there is no obvious correlation of ΔV^* with leaving ligand volume for aquation of substituted phen complexes. In another reacting system which has a dissociative, D or S_N1 (lim) mechanism, $[Fe(CN)_5L]^{3-}$ + CN^-, a more systematic variation of leaving group ligand, (L) (where L is a substituted pyridine or pyrazine), is possible. But there is a distinct lack of correlation between activation volume and volume of leaving ligand or the angle subtended at the complex ion by comparable extremities of L.[23] Others report a similar conclusion.[24] These reactions and results of the investigations of them have been the subject of a review.[25] Overall, the combinations of mechanistic contributions which give rise to particular ΔV^* values are far from being well understood. There is much support for mechanistic discrimination from interpretation of ΔV^* data,[19,26] and for dissociation of iron(II)–diimine complexes by nucleophilic attack, the rate law and the magnitudes of ΔH^* and ΔS^* support a different mechanism from that for aquation (dissociative). However, there remains some uneasiness that indeed a simple associative mechanism is applicable. In base hydrolysis reactions of cobalt(III) complexes, a conjugate base (CB) mechanism has been proposed[27] and is generally accepted.[28] The ligands used in the studies of base hydrolysis of iron(II) complexes are of a different character, and in any event, no experimental evidence supports a CB mechanism for these complexes, except for the variant expressed in the Gillard mechanism.[3] Therefore, although ΔV^* in this case does not provide unequivocal mechanistic discrimination, the experiments reported are conducted under conditions where second order kinetics are observed (solvolysis and higher order terms are not significant), yielding an associative term in the rate law. The magnitudes of ΔS^* and ΔH^* for base hydrolysis are different from those for aquation, and these two key results represent a preponderance of support for the simplest consistent scheme, i.e., bimolecular, with dominant loss of electrostricted water contributing to positive ΔV^* values. It is conceivable that other experimental methods will yield information that reveals further mechanistic subtlety with a consequent need for further review of the accumulated results.

TWO-STEP DISSOCIATION IN BASIC SOLUTION

The reactions of $Fe(ppsa)_3^{4-}$ with both cyanide and hydroxide yield results which are tangential to the overall thrust of this discussion, but nevertheless warrant inclusion, as some pressure dependent kinetic and equilibrium measurements have been reported.[4c] These reactions are indicative of what may be termed a favorable case in which an intermediate in the overall dissociation process can be detected. Since the intermediate is not as labile as in other systems, both an equilibrium constant for its formation and a rate constant for the subsequent intramolecular reorganization step can be measured. The intermediate thus comports with that postulated by Gillard,[3] and when hydroxide is the attacking nucleophile, the equilibrium constant is 3.5 in a aqueous medium, and, respectively, 16 and 230 in 50% methanol and 50% DMSO, at 291 K. Reaction of $Fe(ppsa)_3^{4-}$ with hydroxide in 33% methanol allows study of the pressure dependence of the equilibrium formation of the intermediate and the subsequent decay of the intermediate, leading to $Fe^{2+}(aq)$, and ultimately $Fe(OH)_3$, and free ligands, and yielding ΔV° and ΔV^* of 0 and -2 cm^3 mol^{-1} for the two processes. These values can be understood if the association process, formation of an intermediate, is accompanied by and compensated for by some loss of electrostricted solvent, presumably from the hydroxide ion hydration shell, and the subsequent step has little volume change, either intrinsic or solvation, upon reaching the transition state. Although the exact nature of the intermediate species is not known, it is clear that there is a significant difference from the reactions of nucleophiles with cationic iron(II)–diimine complexes reported here, where no intermediates are detected or postulated, and ΔV^* for the single kinetic process observed in our laboratory is from $+10$ to $+16$ cm^3 mol^{-1}.

Attempts to probe further the effect of negatively charged complex ions upon the mechanism of dissociation, using $Fe(fer)_3^{4-}$ (see Scheme 1), revealed a two step process when using a hydroxide[4d] ion as the nucleophile. At low concentrations of hydroxide, but still well in excess of $[Fe(fer)_3^{4-}]$, the first step is second order overall and is conveniently measured using the stopped-flow technique. The presence of a reverse reaction component in the overall rate law precludes unequivocal information being obtained from a high pressure kinetics study, were it to be conducted. A second slow step is first order in hydroxide concentration, again indicating a kinetic indistinguishability problem when trying to analyze activation parameters. An acid-mediated dissociation of $Fe(fer)_3^{4-}$ produces a rate constant for aquation which shows that the negative complex ion is only slightly more labile than the cationic $Fe(bpy)_3^{2+}$, but it is considerably less reactive than $Fe(btz)_3^{2+}$. Although the mechanism in detail must be different, the iron(II)–tris complex of ferene dissociates in the presence of hydroxide in two distinguishable steps, as does the iron(II)–tris complex of ferrozine.

The presence of negatively charged groups as strong electron withdrawing groups on the ligand is thought to provide appropriate conditions within the ligand to attract attack by a nucleophile. However, upon using $\mathrm{Fe(fertri)}_3^{2+}$, where fertri is fer without sulfonato groups, dissociation in basic solution, with added solvent to maintain a solution, also has two distinct kinetic steps.[29] Therefore, features of these reactions are far from being completely understood.

ACTIVATION VOLUMES: MIXED SOLVENTS

Turning to solvent effects on activation volumes, the main feature of these is that in a given series of mixed solvents, there is a marked difference in behavior according to the nature of the ligand. Figure 2 shows the trends for several of these complexes in methanol–water mixtures. Clearly these are not determined solely by hydroxide desolvation. For the smaller ligands (gmi, hxsb) the trend is towards the "gas phase" value of $-10\ \mathrm{cm^3\ mol^{-1}}$, but for the larger ligands, particularly $\mathrm{Me_2bsb}$, the tendency is to move even further away from this estimated value for the solventless system. It may be that hydroxide desolvation dominates in the former case (and in this connection it is interesting that ΔV^* for $\mathrm{Mo(CO)_4(bpy)} + \mathrm{CN^-}$ in DMSO is $-9\ \mathrm{cm^3\ mol^{-1}}$);[13a] there will be no significant $\mathrm{CN^-}$ desolvation in forming this transition state, but the bulkiness of ligands such as $\mathrm{Me_2bsb}$ dominates in the latter. But it is difficult to see how ΔV^* can increase by so much on going from water to methanol-rich mixtures, unless the favorable solvation of the very hydrophobic leaving ligand leads to a longer metal–ligand extension on transition state formation in the presence of large proportions of methanol. The dependence of ΔV^* for dissociative solvolysis in methanol–water mixtures, for which no data are available yet, would shed light on this hypothesis. Trends in ΔV^* for base hydrolysis observed in methanol–water mixtures are duplicated, with logical shifts as the hydrocarbon moiety of the alcohol increases, for other mono-ols (Table II). The observations, likewise, are not entirely comprehensible in a specific sense. However, other insights emerge.

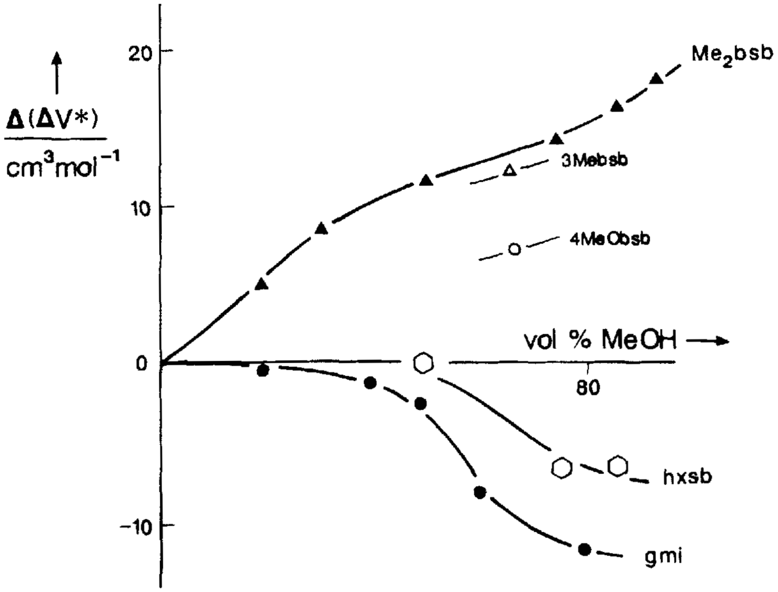

FIGURE 2 Volume of activation versus volume % of CH_3OH for base hydrolysis of several iron(II)–diimine complexes at 298 K. The ordinate axis values are shown as differences from the volume of activation in water.

TABLE II

Activation volumes for dissociation of iron(II)–diimine complexes by hydroxide ion in aqueous mono-ols at 298 K

Complex[a]	ΔV^{*ab} cm^3/mol^{-1}			
	H_2O	67% CH_3OH	17% t-C_4H_9OH	50% t-C_4H_9OH
Fe(Me$_2$bsb)$_3^{2+}$	11.1	25[c]	27	21[d]
Fe(3Mebsb)$_3^{2+}$	13.6	26		
Fe(4MeObsb)$_3^{2+}$	12.0	19		
Fe(hxsb)$_3^{2+}$	13.4	6[c]	14	−4.2
Fe(gmi)$_3^{2+}$	16.7	8.1	12.2	14.6
Fe(Me$_2$tsb)$_2^{2+}$	6	19		

[a] Ligands and abbreviations defined in the text and in Scheme 1.

[b] Errors on measured ΔV^* values are typically in the range of ±5 to ±15%.

[c] 75% CH_3OH.

[d] 40% t-C_4H_0OH.

Both for large and small leaving ligands, ΔV^* trends in a series of alcohol–water solvent mixtures indicate an important role for solvent structure. Figure 3 shows how, for base hydrolysis of Fe(gmi)$_3^{2+}$, the ΔV^* values fall away from the value in water at mole fractions corresponding to compositions of maximum solvent structuring by the respective alcohol cosolvents. A similar pattern has been established for base hydrolysis of the Fe(hxsb)$^{2+}$ cation. Figure 4 shows the pattern for the Me$_2$bsb complex. The large maximum at mole fractions around 0.05 t-butyl alcohol is striking; ΔV^* for base hydrolysis of the analogous bis–terdentate complex Fe(tsbMe$_2$)$_2^{2+}$ also shows a large increase on going from water[30] to 17% t-butyl alcohol (Fig. 4). Such a marked effect here must surely be attributable to the changing balance between solvent–solvent and solute–solvent interactions, maximized for a large hydrophobic ligand leaving into solvent mixtures with the biggest structural modifications. Due to various preparative and technical difficulties with these particularly bulky diimine complexes, we propose to investigate ΔV^* vs. mole fraction of t-butyl alcohol trends for bulky hydrophobic leaving groups for ligand substitution in pentacyanoferrates (II), Fe(CN)$_5$L^{3-}.

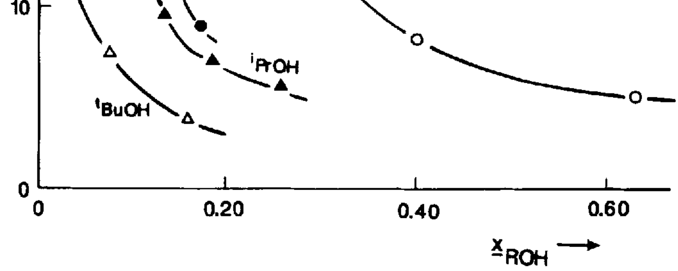

FIGURE 3 Volume of activation versus mole fraction of cosolvent for base hydrolysis of Fe(gmi)$_3^{2+}$ at 298 K.

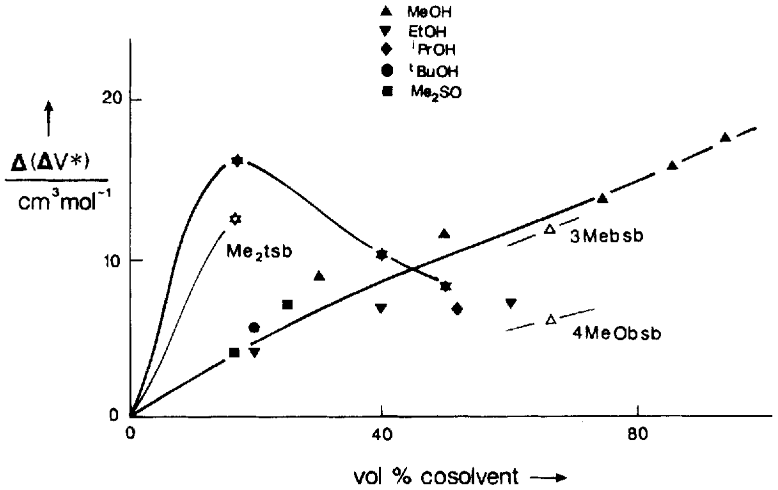

FIGURE 4 Volume of activation versus volume % of cosolvent for base hydrolysis of several iron(II)–diimine complexes at 298 K. The ordinate axis values are shown as differences from the volume of activation in water. A selection of points for related complexes (base hydrolysis) is included in the figure.

We are endeavoring to ascertain if a relationship exists between various geometrical features of departing ligands and measured ΔV^*. Earlier work pointed to the absence of any obvious correlation.[22,23] Others are recognizing the potential significance of cone angles in various metal complexes.[32]

CONCLUDING COMMENTS

On the basis of the rate law and thermal and pressure derived activation parameters, aquation of Fe(X-1,10-phen)$_3^{2+}$ complexes occurs by a dissociative mechanism. However, there is no obvious correlation of the magnitude of ΔV^* with leaving group property or with scavenging agent, which suggests that I_d character is less likely than D character. Further insight may be obtained by determining ΔV^* in aqueous mono-ol mixtures since hydrophobic or hydrophilic substituents upon 1,10-phenanthroline should be differently solvated as the ligand extends into the solvent in the transition state; for example, as substituents -Br and -CH_3 are virtually equal sterically, but dissimilar in solvation property. Experiments with a greater range of ligands could provide valuable information. A thorough study of the effect of ionic strength upon ΔV^* could be informative; however, the dependence, if any, is of a particularly specific nature to the individual reaction.[14b,33] There are attendant frustrations in attempting to understand exactly how ionic strength affects ΔV^* in electron transfer reactions as well where in some cases different catalytic effects are reported for some "inert" ions,[34] adding to complications for the rate law and interpretation of measured activation parameters.

Base hydrolysis of Schiff-base complexes of iron(II) occurs by an associative mechanism. This conclusion is based upon the literature of rate law and activation parameters for all the complexes studied, and the difference from comparable expressions or parameters for aquation. Results for nucleophilic attack by a cyanide ion could also be interpreted as consistent with an associative mechanism. Nevertheless, some questions remain. The measured positive ΔV^* values for basic hydrolysis in water are explained[13b] on the basis of a volume compression for the intrinsic component being overshadowed by a large and reasonably constant (i.e., almost independent of ligands bound to the iron(II) center)[14b] volume increase due to loss of electrostricted solvent from the uninegative incoming nucleophile. Differences in volume of the iron(II) complexes as hydration is perturbed upon reaching the transition state are minor. The values of ΔV^* for OH^- and CN^- attack are very similar, yet $\bar{V}$ for the two ions is significantly different.[20,21] However, there are few direct comparisons of ΔV^* values for reactions involving CN^- and OH^-. This point may be worthy of further investigation. Currently we are examining the properties of other ligands which would potentially form complexes suitable for obtaining informative and pertinent kinetics results.

Although detection of an intermediate has been possible in some cases,[3,4c,4d] the evidence cited therein, regarding the site of nucleophilic attack (direct at iron–nitrogen, or first at an electropositive ligand site) is circumstantial. The detection of an intermediate and the observation in some cases of two-step dissociation kinetics are not unequivocally diagnostic of the mechanism, but together with the form of the rate laws indicate that base hydrolysis of and cyanide reaction with these complexes proceed associatively. The differences of variation of ΔV^* for base hydrolysis in mixed solvents depend upon ligand hydrophilic/hydrophobic character.[13b,13c,14b,30] In general, ΔV^* values veer toward the gas-phase value for the least hydrophobic ligands, and undergo considerable increases in magnitude for the most hydrophobic ligands, as the cosolvent content increases. The trends (ΔV^* vs. mole fraction of cosolvent) are not always predictable, and the interplay between solvation contribution to ΔV^* and mixed solvent structure at particular compositions is far from being fully understood. Therefore, quantitative interpretation of these trends is not yet possible. Calculations may prove helpful in this context.[21]

Recently, a different method based experimentally on kinetic data and surface tension measurements[35] has been employed to obtain ΔV^* values. So far this method has been applied to the substitution reactions of CN^- at pentacyanoferrate (II) complex ions. It has been pointed out that ΔV^* obtained indirectly from surface tension measurements may provide different information from the ΔV^* values obtained from high pressure kinetics in some circumstances. We will continue to study the validity of application of this approach to iron (II)–diimine complex dissociation. In principle, information on possible intermediates during complex dissociation could come through the use of techniques such as NMR spectroscopy, but, as yet, while sensitivity and scope are much improved since early efforts, definitive information is not realizable.

The fundamental rate laws and reaction mechanisms of acid aquation and base hydrolysis of $Fe(bpy)_3^{2+}$ and $Fe(phen)_3^{2+}$ in aqueous solution were established in pioneering work during the period from the late 1940's to the mid-1960's. Subsequently, attention turned to other, but similar, complexes, and when a pseudo-base mechanism for base hydrolysis in some cases was postulated, a whole new vista of interest in these reactions was opened. This provoked a lack of unanimity among investigators on the mechanistic aspect of dissociation, a controversy not yet resolved. The pressure variable assumed a pivotal role in the study of reactions of these complexes from the late 1970's until now. Solvation information, now obtained from high pressure kinetics, had earlier been probed by the approach of making appropriate kinetic and thermodynamic measurements in solvents and solvent mixtures. While advances in understanding these reaction pathways have been incremental in recent years, it is undeniable that much progress has been reported. We look forward eagerly to the development of even firmer mechanistic conclusions and insight into the details of solvation influences which we are confident will come from a combination of spectroscopic and kinetics methods and suitable calculations.

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