

Volumes of Activation for Aquation of Tris(1,10-phenanthroline)iron(II) Complexes in Aqueous Solution

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Activation volumes for aquation of the tris(1,10-phenanthroline)iron(II) cation and of its 5-nitro- and 4,7-dimethyl derivatives in 1M-H₂SO₄ at 35 °C are +15.4 ± 0.4, +17.9 ± 0.3, and +11.6 ± 0.6 cm³ mol⁻¹ respectively. These values are consistent with a dissociative mechanism for aquation of these complexes.

NUMEROUS studies of the kinetics of substitution reactions of low-spin iron(II) complexes, both in aqueous and in aqueous-organic media, have been reported during the past three decades.^{1,2} The mechanism of aquation of these complexes is usually assumed to be dissociative in nature, but some observations, particularly relating to reactivity trends for aquation in mixed solvents, are not inconsistent with significant associative character.^{3,4}

The determination of activation volumes is a well established approach to the diagnosis of mechanisms of substitution reactions in organic chemistry.⁵ This method is particularly useful for reactions involving uncharged leaving (entering) groups, in which situations the interpretation of observed activation volumes is not complicated by solvent electrostriction effects. Recently the determination of activation volumes for some substitution reactions of transition-metal complexes has proved informative. In particular the demonstration of negative volumes of activation for water exchange at the [Cr(OH₂)₆]³⁺ (ref. 6) and [Cr(NH₃)₅(OH₂)]³⁺ (ref. 7) cations, but of a positive volume of activation for water exchange at the [Co(NH₃)₅(OH₂)]³⁺ cation,⁸ has indicated considerable associative character to these substitutions at chromium(III) in contrast to the established dissociative mode of substitution at cobalt(III).

We have therefore determined volumes of activation for the aquation of the tris(1,10-phenanthroline)iron(II) cation and its 5-nitro- and 4,7-dimethyl derivatives, [Fe(phen)₃]²⁺, [Fe(5-NO₂phen)₃]²⁺, and [Fe(4,7-Me₂phen)₂]²⁺, to ascertain whether the mechanisms for aquation of these complexes are predominantly associative or dissociative in character and whether this associative or dissociative character varies significantly with substitution of the phen ligands. This latter aim was prompted by observations⁹ on the solvolysis of aromatic sulphonyl chlorides in which a trimethyl-substituted chloride is considered to solvolyse through a dissociative (S_N1) path whilst other substituted chlorides proceed through an associative (S_N2) path.

† 1M = 1 mol dm⁻³; 1 bar = 10⁵ Pa.

¹ See, for example, 'Inorganic Reaction Mechanisms,' ed. J. Burgess, Chem. Soc. Specialist Periodical Report, London, 1971, vol. 1, pp. 176—177, 186—187; 1972, vol. 2, pp. 168—169, 173, 182; 1974, vol. 3, pp. 214—217, 243—244; C. H. Langford and V. S. Sastri, 'Reaction Mechanisms in Inorganic Chemistry,' ed. M. L. Tobe, M.T.P. Internat. Rev. Sci., vol. 9, Butterworths, London, series 1, 1971, p. 252.

² F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' Wiley, New York, 1967, 2nd edn., pp. 218—219.

³ J. Burgess, *J. Chem. Soc. (A)*, 1968, 1085.

EXPERIMENTAL

Aqueous solutions of [Fe(X-phen)₃]²⁺ and sulphuric acid were mixed to yield reaction mixtures 10⁻⁴M in [Fe(X-phen)₃]²⁺ and 1M in H₂SO₄. Under these conditions aquation of the highly coloured cations is complete and the progress of aquation was monitored continuously at 510 nm with an SP 800 spectrophotometer with scale-expansion facilities linked to a Rikendenki pen recorder. At 35 °C, reaction half-times varied from 4 min {for [Fe(5-NO₂phen)₃]²⁺ at atmospheric pressure} to 180 min {for [Fe(4,7-Me₂phen)₃]²⁺ at 1.5 kbar pressure}.† Rate coefficients were evaluated from the continuous optical absorbance-time records using the Guggenheim method with a fixed time interval of 2—2.5*t*₁. All reactions were followed for at least four half-times and excellent linearity of the first-order Guggenheim plots was observed.

Reactions were conducted in a high-pressure vessel fitting into the normal cell compartment of the SP 800 spectrophotometer. The pressure vessel was maintained at 35 °C by thermostatted water circulated through channels in the body of the steel vessel. Sapphire windows in the pressure vessel were aligned along the optical axis of the spectrophotometer to permit continuous spectrophotometric observation of the pressurized reaction mixture. A specially designed mixer enabled the two separated reactant solutions to be first located in the 1 cm path length cell within the high-pressure vessel, the two solutions brought to the desired pressure and temperature, and complete mixing was then achieved in less than 1 s by operation of an electromagnetically driven diaphragm mixer inside the cell. The first design of this high-pressure mixing cell limited operations to 1.8 kbar maximum pressure but this available pressure range still permitted accurate evaluation of the volume of activation.

RESULTS

The rate of aquation of all three phen complexes was retarded markedly by the application of pressure. Table I summarizes mean values of the rate coefficients determined at different pressures and the number of replicate determinations at each pressure. The data for all three complexes are accommodated adequately by the simple relation between the pressure variation of the rate coefficient and the volume of activation, Δ*V*[‡] [equation (1)]. This is

⁴ J. Burgess, *J. Chem. Soc. (A)*, 1969, 1899.

⁵ See, for example, E. Whalley, *Adv. Phys. Org. Chem.*, 1964, **2**, 93; *Ann. Rev. Phys. Chem.*, 1967, **18**, 205; W. J. le Noble, *Progr. Phys. Org. Chem.*, 1967, **5**, 207.

⁶ D. R. Stranks and T. W. Swaddle, *J. Amer. Chem. Soc.*, 1971, **93**, 2783.

⁷ T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, 1972, **94**, 8357.

⁸ H. R. Hunt and H. Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 2642.

⁹ M. L. Tonnet and A. N. Hambly, *Austral. J. Chem.*, 1971, **24**, 703.

shown in Figure 1 where in each case $\ln(k_P/k_1)$ is a linear function of the applied pressure, at least up to 1.7 kbar.

$$(\partial \ln k / \partial P)_T = -\Delta V^\ddagger / RT \quad (1)$$

The volumes of activation for aquation of the three phen complexes were therefore deduced using equation (1). Values of ΔV^\ddagger , together with their standard deviations calculated by a standard least-squares routine, are collected

TABLE 1

Variation of average first-order rate coefficients (k/s^{-1}) for aquation of tris(1,10-phenanthroline)iron(II) complexes (1M-H₂SO₄, at 35 °C) with applied pressure (P/bar) together with standard deviations of average rate coefficients (σ) and the number of replicate determinations (n) at each pressure

P	1	345	690	1 035	1 380	1 725
phen complex						
10 ⁵ k	36.7		24.5		16.1	
σ	1.8		0.4		0.2	
n	6		4		5	
5-NO ₂ phen complex						
10 ⁵ k	240	187	143	121	91.4	71.2
σ	8	4	0	2	3	1
n	9	3	3	4	3	3
4,7-Me ₂ phen complex						
10 ⁵ k	11.1	9.5	8.4	7.12	6.14	
σ	0.5		0.8	0.1	0.6	
n	10	1	2	3	6	

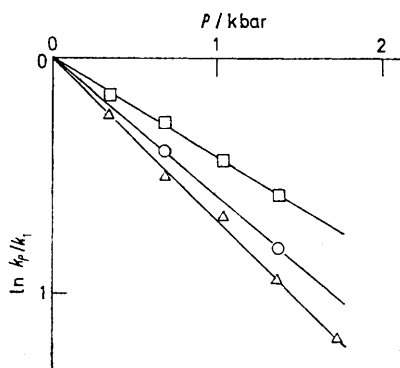


FIGURE 1 Pressure variation of rate coefficients for aquation of $[\text{Fe}(\text{X-phen})_3]^{2+}$ cations: X = 5-NO₂ (Δ), H (\circ), and 4,7-Me₂ (\square)

TABLE 2

Values of volumes of activation ($\Delta V^\ddagger/\text{cm}^3 \text{mol}^{-1}$) for aquation of substituted tris(1,10-phenanthroline)iron(II) complexes (1M-H₂SO₄, at 35 °C) and upper limits for the corresponding compressibility coefficients of activation ($\Delta\beta^\ddagger/\text{cm}^3 \text{mol}^{-1} \text{kbar}^{-1}$)

Substituent	ΔV^\ddagger	$\Delta\beta^\ddagger$
None	15.4 ± 0.4	< 0.6
5-NO ₂	17.9 ± 0.3	< 0.4
4,7-Me ₂	11.6 ± 0.6	< 0.9

in Table 2. A possible pressure dependence of the volume of activation itself cannot be tested adequately with the

* In the case of the reaction with hydroxide, it has recently been suggested that hydroxide may attack at the phen ring rather than at the iron atom (R. D. Gillard and J. R. Lyons, *J.C.S. Chem. Comm.*, 1973, 585).

¹⁰ R. Davies, M. Green, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1171.

¹¹ J. H. Baxendale and P. George, *Trans. Faraday Soc.*, 1950, 46, 736.

present data determined over a rather small pressure range. Nevertheless, upper limits may be placed on the values of the compressibility coefficient of activation defined as $\Delta\beta^\ddagger = -(\partial \Delta V^\ddagger / \partial P)_T$; these upper limits are also collected in Table 2.

DISCUSSION

Despite the large number of kinetic studies of substitution reactions of low-spin iron complexes, especially of $[\text{Fe}(\text{phen})_3]^{2+}$ and its derivatives, the mechanism of aquation of these complexes is not unequivocally established. Analogy with substitution mechanisms for complexes of the other much studied low-spin d^6 cobalt(III) cation where I_d and D mechanisms operate, suggests dissociative activation at these iron(II) complexes. The acid dependence of aquation rates of the $[\text{Fe}(\text{bipy})_3]^{2+}$ cation (bipy = 2,2'-bipyridyl) is also commonly explained in terms of a D mechanism,^{2,10} although an early discussion of this reaction hints at the possibility of the incorporation of incoming water into the transition state.¹¹ On the other hand, rate laws and activation parameters for reactions of many complexes of the $[\text{Fe}(\text{phen})_3]^{2+}$ type indicate bimolecular attack by cyanide¹² and by hydroxide¹³ at iron(II) in these reactions.* Water will be much more reluctant than either cyanide or hydroxide to attack at iron(II), but, in view of its relatively much higher concentration and close proximity to the iron atom,¹⁴ the possibility of some iron-incoming water interaction in the transition state for aquation of these complexes cannot be summarily excluded.

Reactivity patterns for aquation of the $[\text{Fe}(5\text{-NO}_2\text{-phen})_3]^{2+}$ and $[\text{Fe}(4,7\text{-Me}_2\text{phen})_3]^{2+}$ cations in mixed aqueous solvents can readily be rationalized in terms of more associative character to aquation of the former complex. This is consistent with the strong electron-withdrawing properties of the 5-nitro-substituent making the iron atom relatively more electropositive and thus more susceptible to nucleophilic attack. Thus in aqueous formic acid solvent mixtures, where water is firmly bound into the solvent structure, aquation rates of the 5-NO₂phen and of the 4,7-Me₂phen complexes both decrease, to a similar extent, as the mol fraction of the formic acid increases. But in aqueous ethanol, where the structure of the water is, except at low mol fractions of ethanol, broken down by the organic co-solvent, aquation rates for the two complexes behave very differently as the solvent composition varies. The aquation rates of the 4,7-Me₂phen complex decrease with increasing mol fraction of ethanol, to parallel the aqueous formic acid trend, but aquation rates of the 5-NO₂phen complex increase with increasing mol fraction of ethanol (at least up to $x_{\text{EtOH}} = 0.17$). This pattern is consistent with the increasing availability of

¹² D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, 84, 706; J. Burgess, *Inorg. Chim. Acta*, 1971, 5, 133; J. Burgess and M. V. Twigg, *J.C.S. Dalton*, 1974, 2032.

¹³ D. W. Margerum, *J. Amer. Chem. Soc.*, 1957, 79, 2728; J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697; G. Nord and T. Pizzino, *Chem. Comm.*, 1970, 1633.

¹⁴ A. Jensen, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1958, 80, 2354.

water for incorporation into the transition state encouraging aquation of the 5-NO₂phen complex by a mechanism of significant associative character, but having little effect on the aquation of the 4,7-Me₂phen complex by a predominantly dissociative mechanism. This type of argument can also be applied to aquation-rate trends reported for variously substituted [Fe(phen)₃]²⁺ cations in aqueous t-butyl alcohol,³ acetonitrile,¹⁵ dioxan,¹⁶ and methanol¹⁷ solvent mixtures. However the observed rate trends could equally well be rationalized simply in terms of variation of the degree of solvation of the initial and/or transition states of a dissociative aquation mechanism.

Activation volumes, rate coefficients, and entropies of activation¹⁸ for aquation of the three iron(II)-phen complexes are collected and compared in Table 3. The

TABLE 3

Kinetic parameters for aquation of [Fe(X-phen)₃]²⁺ cations in aqueous solution. Values of *k* and Δ*S*[‡] are at 25 °C (these and the Δ*H*[‡] values are from ref. 18); values of Δ*V*[‡] are at 35 °C

X	10 ⁵ <i>k</i> /s ⁻¹	Δ <i>H</i> [‡] /kcal mol ⁻¹	Δ <i>S</i> [‡] /cal K ⁻¹ mol ⁻¹	Δ <i>V</i> [‡] /cm ³ mol ⁻¹
H	7.3	29.3 *	+21	+15.4 ± 0.4
5-NO ₂	49	28.0 *	+21	+17.9 ± 0.3
4,7-Me ₂	2.2	27.8 *	+13	+11.6 ± 0.6

* Standard deviations are in each case ±0.2 kcal mol⁻¹; the corresponding standard deviations in Δ*S*[‡] are ±0.7 cal K⁻¹ mol⁻¹.

high values for the activation enthalpies, several kcal mol⁻¹ higher than for cyanide or hydroxide bimolecular attack, are consistent with a dissociative mechanism; the positive activation entropies are easier to accommodate in a dissociative than an associative scheme; but it is the markedly positive activation volumes which give the clearest indication of the operation of a dissociative mechanism for the aquation of all three complexes. It is difficult to see how more than an insignificant degree of associative character can be consistent with the markedly positive values; compare, for example, a volume of activation of only +1.2 cm³ mol⁻¹ for water exchange with the [Co(NH₃)₅(OH₂)]³⁺ cation by a presumed⁸ dissociative-interchange mechanism or the even more positive value¹⁹ Δ*V*[‡] = +14.3 cm³ mol⁻¹ for dissociative isomerization of *trans*-[Co(en)₂(OH₂)₂]³⁺ to the *cis*-isomer (en = ethylenediamine).

However the assignment of predominantly dissociative character to the aquation process is best justified not by analogy but by a quantitative estimate of the probable changes in the dimensions of the [Fe(phen)₃]²⁺ cation which correspond to the measured value Δ*V*[‡] = +15.4 cm³ mol⁻¹. For this purpose it will be assumed that, when a transition state is generated by dissociation of one phen ligand, all the volume increase

arises from motion of that single bidentate ligand; it is assumed that no compensatory volume effect arises from any shortening of the other Fe-N bonds to the remaining two ligands. A convenient representation of a bidentate phen ligand in the ground state is given in Figure 2: the stated dimensions are based on an Fe-N bond distance²⁰ of 1.97 Å and accepted covalent bond lengths in the rings; all peripheral hydrogen atoms are assigned van der Waals radii of 1.2 Å and the half-thickness²¹ of the rings is 1.85 Å. This crude description of the co-ordinated ligand corresponds to a 'polygonal sandwich' of 11.5 Å maximum length and 3.70 Å in thickness.

One possible mode for dissociative release of a bidentate phen chelate would be 'one-ended dissociation' in which the flat phen ring pivots about one nitrogen atom whilst the other Fe-N bond is extended. However this commonly postulated mechanism seems to be

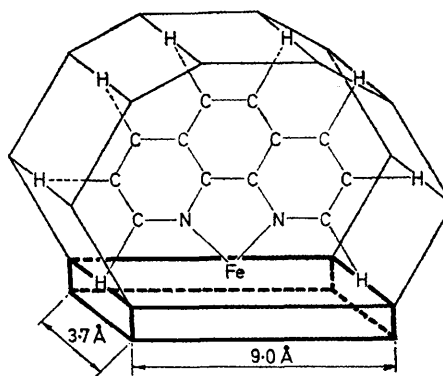


FIGURE 2 Schematic representation of a bidentate phen chelate in [Fe(phen)₃]²⁺. The dimensions are based on bond lengths and van der Waals radii discussed in the text

precluded for [Fe(phen)₃]²⁺ because of severe steric restrictions. In the ground state of [Fe(phen)₃]²⁺, hydrogen atoms on carbon atoms 2 and 9 of one phen ring are virtually in van der Waals contact with the adjacent phen rings. Motion of either of these hydrogen atoms, as required by a one-ended pivot motion, may not occur. Likewise a twisting mode combined with a pivot mode is also precluded by the same steric restrictions.

Consequently the most-probable dissociative mode for [Fe(phen)₃]²⁺ is one involving simultaneous stretching of both the Fe-N bonds of one bidentate chelate. Using the dimensions assumed above for [Fe(phen)₃]²⁺ a positive volume change of +15.4 cm³ mol⁻¹ for formation of an activated complex may be generated by simultaneous extension of both Fe-N bonds from 1.97 Å in the ground state to 2.58 Å in the transition state. This simple model assumes that the leaving phen ligand does not tilt, but remains in the plane defined by its two nitrogen atoms and the iron atom throughout the

¹⁹ D. R. Stranks, *Pure Appl. Chem.*, 15th Internat. Conf. Coordination Chem., 1974, **38**, 303.

²⁰ A. Zalkin, D. H. Templeton, and T. Veki, *Inorg. Chem.*, 1973, **12**, 164.

²¹ L. Pauling, 'Nature of the Chemical Bond,' Cornell University Press, Ithaca, N.Y., 3rd. edn., ch. 7.

¹⁵ J. Burgess, *J. Chem. Soc. (A)*, 1970, 2351.

¹⁶ J. Burgess, F. M. Mekhail, and E. R. Gardner, *J.C.S. Dalton*, 1973, 1335.

¹⁷ L. Seiden, F. Basolo, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1959, **81**, 3809.

¹⁸ J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1963, 5752.

dissociative step. This rather large bond extension of 0.61 Å does not correspond however to a state of virtual dissociation of the Fe and N atoms in the transition state; a state of complete dissociation would be reached when the component atoms were just separated by the sum of their respective van der Waals radii or a distance of 2.05 (Fe) + 1.50 (N) = 3.55 Å. (Here the van der Waals radius of iron of 2.05 Å is obtained by extrapolation of the accepted radii for As, Se, and Br in the same period as Fe; the estimate of 2.05 Å for Fe is 0.82 Å greater than the covalent radius of Fe, which difference is close to the usual²¹ difference between van der Waals and covalent radii.) Therefore the extension of the Fe-N bonds in the transition state from 1.97 to 2.58 Å represents $(2.58 - 1.97)/(3.55 - 1.97) = 39\%$ of the total extension necessary for complete dissociation. It is significant that this magnitude of Fe-N bond extension is too small to permit potential water molecules approaching bonding distances with the Fe core, thereby confirming our proposition that the positive ΔV^\ddagger values reflect primarily dissociative processes without being offset by some associative contribution from an incoming water nucleophile. We show below that analogous dissociative mechanisms apply to the two substituted phen complexes.

A logical consequence of the operation of a dissociative mechanism for the aquation of these three complexes is the expectation of a correlation of kinetic parameters with thermodynamic stability parameters, of rate constants with stability constants, and of activation enthalpies with enthalpies of complex formation. Unfortunately there are insufficient thermochemical data available, especially for the substituted complexes, for a complete test of these correlations, but what tests are possible are satisfactory. Thus the rates of aquation (Table 3) parallel the respective $\log_{10} \beta_3$ values ($\log_{10} \beta_3$ for the 5-NO₂phen complex is 15.64,²² for the unsubstituted complex 20.22,²³ and for the 4,7-Me₂ complex 23.1²⁴). Whereas these rates and stability constants correlate with the electron-withdrawing and -releasing power of the substituents, as measured for instance by the ligand pK_a values, activation enthalpies for aquation of substituted $[\text{Fe}(\text{phen})_3]^{2+}$ cations do not.²⁵ Interestingly, and reassuringly for our present mechanistic proposal, the enthalpies of formation (ΔH_f°) of substituted $[\text{Fe}(\text{phen})_3]^{2+}$ cations also show a similar irregularity. The enthalpy of formation of the 4,7-Me₂phen complex is not known, but that for the 5,6-Me₂phen complex ($-30.8 \text{ kcal mol}^{-1}$)²⁶ is, like that for the 5-NO₂ complex ($-25.2 \text{ kcal mol}^{-1}$),²² less than that for the unsubstituted complex ($-31.3 \text{ kcal mol}^{-1}$).^{23,*} In view of the provenance of these enthalpies of complex formation from the temperature dependence of stability constants rather than from direct calorimetric determin-

ations, and of their stated standard deviations, this kinetic-thermodynamic enthalpy correlation provides only a modicum of support rather than unequivocal proof of our proposal of dissociative aquations of all three complexes.

Nevertheless the combined weight of evidence, centred on the positive ΔV^\ddagger values, points to primarily dissociative mechanisms for all three $[\text{Fe}(\text{X-phen})_3]^{2+}$ complexes. There are, however, significant differences in the ΔV^\ddagger values for these three complexes and factors which might contribute to these differences include the relative size of the complexes, specific solvent interactions, and the degree of bond breaking in the transition states. The different intrinsic sizes of the three complexes are unlikely to be major contributors to the ΔV^\ddagger differences. The van der Waals radius of the methyl group (2.0 Å) is only very slightly larger than the half-thickness of the phen ring (1.85 Å) so that the effective thickness of the 'polygonal sandwich' for $[\text{Fe}(4,7\text{-Me}_2\text{phen})_3]^{2+}$ is virtually the same as for $[\text{Fe}(\text{phen})_3]^{2+}$. Motion of a 4,7-Me₂phen ring into the solvent to generate a dissociated activated complex would therefore generate, for an equal increase in Fe-N bond distance, the same ΔV^\ddagger value as for an unsubstituted phen ring. Moreover, ΔV^\ddagger for $[\text{Fe}(4,7\text{-Me}_2\text{phen})_3]^{2+}$ aquation is smaller than ΔV^\ddagger for $[\text{Fe}(\text{phen})_3]^{2+}$ aquation. In the case of $[\text{Fe}(5\text{-NO}_2\text{phen})_3]^{2+}$ the nitro-groups should be coplanar with the phen rings. The van der Waals radius of the oxygen atom of the NO₂ group (1.40 Å) is less than the half-thickness of the ring (1.85 Å). Motion of a 5-NO₂phen ring into the solvent would therefore generate, for equal Fe-N bond extensions, the same ΔV^\ddagger value as for $[\text{Fe}(\text{phen})_3]^{2+}$.

The significant differences between the ΔV^\ddagger values for the three iron(II) complexes could arise from different substituent-solvent interactions or from different degrees of bond breaking in the transition state. Thus, for example, water interaction with the electronegative oxygen atoms of the NO₂ group very likely increases the effective thickness of the NO₂ group in solvent water. However any such hydrogen-bonded water molecules would be located in a solvent zone in which free motion of adjacent water molecules is possible. If a 5-NO₂phen ring with associated water molecules were to sweep out a volume to form a dissociated transition state, then it seems very probable that other free solvent water molecules could move in behind NO₂-bonded water molecules and offset any contribution to the overall ΔV^\ddagger value. This line of reasoning assumes that the degree of hydration of the dissociating 5-NO₂phen ring is identical in the ground and transition states. This assumption (which might be tested by suitable studies in mixed solvents) would lead to the conclusion that specific water interactions with the substituted phen

* 1 cal = 4.184 J.

²² S. C. Lahiri and S. Aditya, *Z. phys. Chem. (Frankfurt)*, 1964, **43**, 282.

²³ S. C. Lahiri and S. Aditya, *Z. phys. Chem. (Frankfurt)*, 1964, **41**, 173.

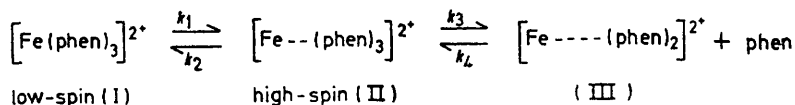
²⁴ D. A. Brisbin and W. A. E. McBryde, *Canad. J. Chem.*, 1963, **41**, 1135.

²⁵ J. Burgess, *J. Chem. Soc. (A)*, 1967, 431.

²⁶ S. C. Lahiri and S. Aditya, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2487.

rings do not contribute significantly to the differences in ΔV^\ddagger values.

On the other hand, the differences in ΔV^\ddagger values for aquation of $[\text{Fe}(\text{X-phen})_3]^{2+}$ complexes can be attributed to differences in the degree of bond breaking in forming the respective activated complexes. Using the same simplified calculations described above for the unsubstituted complex, the bond stretching necessary to reproduce the observed ΔV^\ddagger values can be estimated;



these estimates are summarized in Table 4. It is not possible to discriminate between dissociative interchange, I_d , or dissociative, D , mechanisms on the basis

TABLE 4

Estimated iron-nitrogen bond extensions ($\Delta l/\text{\AA}$) and degree of bond breaking ($D/\%$) for dissociative formation of activated complexes in the aquation of $[\text{Fe}(\text{X-phen})_3]^{2+}$ cations

X	Δl	D
H	0.61	39
5-NO ₂	0.72	46
4,7-Me ₂	0.45	28

of these estimated degrees of bond breaking in the transition state, but, until evidence of competition for an intermediate of reduced co-ordination number is adduced, then an I_d description for the aquation mechanism seems appropriate. It is significant that the bond extensions, calculated from our simple model, range from 0.45 to 0.61 \AA , and are thus all much less than that which would be required for entry of an incoming water nucleophile (effective diameter 2.75 \AA) into a position of significant bonding to the central iron atom.

A further consideration in the role of water in the aquation reactions concerns water molecules located in the large clefts between the three phen rings. It is conceivable that this water might be squeezed out from the clefts due to motion of a phen ring thereby contributing to the overall positive ΔV^\ddagger values. The movement of water from a strongly electrostricted zone about a cation, in which water is highly compressed, into the bulk solvent, in which water is under normal compression, should entail¹⁹ a significant change in the compressibility coefficient of activation, $\Delta\beta^\ddagger$. The movement of 1 mol of water from the secondary sphere of a cation into bulk water should give rise to curved plots of $\ln(k_p/k_1)$ against pressure and the pressure dependence of ΔV^\ddagger should be $\Delta\beta^\ddagger = 0.72 \text{ cm}^3 \text{ mol}^{-1} \text{ kbar}^{-1}$. Whilst the present studies were limited in their available pressure range, it seems very likely from the upper limits of $\Delta\beta^\ddagger$ given in Table 2 that no more than

one water molecule, if any at all, can contribute to the overall positive ΔV^\ddagger values which are observed.

The two-bonded dissociative mode proposed for aquation is probably related to a mechanism²⁷ proposed for the racemization of $[\text{Fe}(\text{phen})_3]^{2+}$, in which a process of bond expansion is postulated to arise from excitation of the low-spin $d^6 \text{ Fe}^{\text{II}}$ system to a high-spin state. This mechanism can be represented by the following micro-states:

Step k_2 can involve intramolecular racemization through a twist process whilst step k_3 ultimately leads to aquation and intermolecular racemization. (In our present studies k_4 is negligible since reactions were conducted in high acid solutions.) In the case of $[\text{Fe}(\text{phen})_3]^{2+}$, k_3 is the dominant term but k_2 is still significant and both modes of racemization proceed with positive entropies of activation. Bond expansion to state (II) is however likely to be comparatively slight since in the conversion of the low-spin 2T_2 state of iron(III) *N,N*-dialkyldithiocarbamates to the high-spin 6A state, a positive volume change of $+3.9 \text{ cm}^3 \text{ mol}^{-1}$ was observed.²⁸ This ΔV value was identified with a general expansion of three bidentates of the FeS_6 cluster by a distance of 0.07 \AA . If only one bidentate chelate were expanded the bond expansion would be *ca.* 0.20 \AA , a value distinctly smaller than that estimated for the aquation process in $[\text{Fe}(\text{phen})_3]^{2+}$. Thus it seems quite likely that the transition state for aquation involves a significant excitation and bond expansion much greater than that for creation of a thermally equilibrated high-spin state.

In summary, these high-pressure studies lead to the conclusion that the aquation of iron(II) phenanthroline complexes in aqueous acidic media proceeds through transition states generated by two-ended dissociation of a phen bidentate ring with neither significant water association to the central iron atom nor significant expulsion of secondary water between the chelate rings. It is likely, but not certain, that this dissociative mechanism will also operate in mixed aqueous solvents, although special solvent interactions, as with $[\text{Fe}(5\text{-NO}_2\text{phen})_3]^{2+}$ in water, plus a structure-breaking solvent may induce alternative reaction modes.

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²⁷ N. R. Davies, *Rev. Pure Appl. Chem.*, 1954, **4**, 66.

²⁸ A. H. Ewald, R. L. Martin, I. B. Roso, and A. H. White, *Proc. Roy. Soc.*, 1964, **A220**, 235.