

it solution for \hat{a} , using the observed K_A values, gives 6.64 and 6.99 for the penta- and hexa-salts, respectively. (The values of $K_A \approx 8$ in acetonitrile in Table II were calculated from the above \hat{a} -values, using equation 3.) As would be expected from the relative sizes of the two ions and the weaker field of the hexa-anion due to a greater spatial distribution of its single charge, the hexa-salt is noticeably less associated than the penta-salt.

TABLE II
DERIVED CONSTANTS

Salt	Solvent	Λ_0	K_A	\hat{a}_A^0	\hat{a}_K^0	\hat{a}_J
5	H ₂ O	67.19 ± 0.01	0	5.49	..	5.2
5	MeCN	169.57 ± .01	(8)	5.61	..	5.62
5	C ₂ H ₄ Cl ₂	70.81 ± .17	2570	5.50	6.64	8.7
6	MeCN	156.35 ± .01	(8)	6.10	..	6.19
6	C ₂ H ₄ Cl ₂	66.94 ± .13	2000	6.32	6.99	9.0

The hydrodynamic radii¹² calculated from the limiting conductances of the penta-salt in three quite dissimilar solvents (water, acetonitrile and ethylene dichloride) agree within a few percent., showing that no special CN-CN interaction (*e.g.*, "selective solvation") occurs in acetonitrile between solvent and anion. The hexa-salt was too low in solubility to be studied in water; the a_A values in acetonitrile and in ethylene dichloride, however, are also in good agreement with each other.

(12) R. M. Fuoss, *Proc. Natl. Acad. Sci., U. S.*, **45**, 807 (1959).

The values of a_A from Λ_0 and of a_J from J agree well for both salts in the solvents of higher dielectric constant, but $a_J > a_A$ in ethylene dichloride. This discrepancy has been noted before¹³ in solvents of low dielectric constant; its origin is suspected to lie in several of the approximations made in deriving the conductance equation¹⁴ which, while valid for large values of D , become less reliable as D decreases below about 20. The values of the contact distance, calculated by any one of the three methods, are large enough, however, to show that the charges on the polycyanions cannot possibly be localized to any one site in the ion.

The salts are colored (penta, yellow; hexa, orange) and also show strong absorptions in the near ultraviolet (molecular extinction coefficients $\epsilon = 2.2 \times 10^5$ for the penta-salt in ethylene dichloride at $\lambda = 417.5 \text{ m}\mu$; $\epsilon = 4.4 \times 10^5$ for the hexa-salt in the same solvent at $\lambda = 469.0 \text{ m}\mu$. These wave lengths correspond to the long wave length members of a double peak in the absorption spectrum). With the thought that ion pair formation might distort the anionic electron distribution, some exploratory measurements were made. The molar extinction coefficient of the penta-salt was, however, found to be unchanged over the concentration range 6.4×10^{-4} to 6.4×10^{-6} , where the fraction of paired ions varies from about 25 to 1%.

(13) E. Hirsch and R. M. Fuoss, *J. Am. Chem. Soc.*, **82**, 1018 (1960).

(14) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 868 (1957); R. M. Fuoss, unpublished calculations.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK]

The Kinetics of the Reactions of Substituted 1,10-Phenanthroline, 2,2'-Dipyridine and 2,2',2''-Tripyridine Complexes of Iron(III) with Iron(II) Ions¹

BY M. H. FORD-SMITH AND N. SUTIN

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The kinetics of the oxidation of iron(II) ions by a number of substituted 1,10-phenanthroline, 2,2'-dipyridine and 2,2',2''-tripyridine complexes of iron(III) have been investigated in both sulfuric and perchloric acid solutions using a rapid-mixing and flow technique. The logarithms of the second order rate constants were found to be linearly related to the average basicity per nitrogen atom of the ligands for oxidations by the unsubstituted and the 5-nitro-, 5-chloro-, 5-phenyl- and 5-methyl-phenanthroline complexes of iron(III). The free energies of activation for the oxidation of ferrous ions by the unsubstituted, the 5-substituted, the 5,6-dimethyl- and the 3,4,7,8-tetramethyl-phenanthroline complexes of iron(III) are linearly related to the standard free energy changes of the reactions. The absence of specific steric effects suggests that the electron-transfer between the iron(III) complex and the ferrous ion takes place in an activated complex in which the ferrous ion has penetrated the space between the phenanthroline groups.

Introduction

The kinetics of the oxidation of iron(II) ions by tris-(1,10-phenanthroline)-iron(III) ions have recently been investigated.² In a comparison of this reaction and several other iron(II) ion oxidations, it was found that the free energies of activation could be linearly related to the standard free energy changes of the reactions. We have extended this work to include the oxidation of ferrous ions by a number of substituted 1,10-phenanthroline, 2,2'-dipyridine and 2,2',2''-tri-

pyridine iron(III) complexes in both sulfuric and perchloric acid solutions. With various groups substituted in the phenanthroline nucleus, it is possible to obtain iron(II) complexes with formal oxidation potentials ranging from 0.81 to 1.25 volts.³ Substitution in the phenanthroline nucleus alters the basicity of the nitrogen atom and hence its electron-donating properties. Since an increase in the electron-donating ability of the nitrogen atom will tend to stabilize the iron(III) complex relative to the iron(II) complex, the formal oxidation potentials of the iron(II) complexes

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, **83**, 70 (1961).

(3) G. F. Smith and W. M. Banick, *Talanta*, **2**, 848 (1959).

should be related to the pK_a of the substituted phenanthrolines, all other things being equal.^{3,4} Such a relationship has been demonstrated for a large number of substituted phenanthrolines.³

A linear relationship between the logarithm of the first order rate constant and both the pK_a of the ligand, and the formal oxidation potential of the iron(II) complex has been demonstrated for the dissociation of a number of 5-substituted phenanthroline complexes of iron(II).⁵ We were interested to see whether a similar relationship exists between the logarithm of the second order rate constant for the oxidation of the iron(II) ions by the substituted phenanthroline complexes of iron(III) and either the pK_a of the ligand or the formal oxidation potential of the iron(II) complex. Such a linear relationship might be expected unless the substituent groups exert specific steric effects.

Experimental

Chemicals.—Either the iron(II) complex or the ligands were obtained from the G. Frederick Smith Chemical Co. In the latter case, the iron(II) complex was prepared by adding an equivalent amount of the appropriate ligand to a solution of ferrous sulfate. The perchlorate of the iron(II) complex was precipitated by adding sodium perchlorate. The iron(III) complex was prepared either by oxidizing a solution of the iron(II) complex in dilute sulfuric acid with lead dioxide or by oxidizing a solution of the iron(II) complex in concentrated perchloric or sulfuric acid with ceric sulfate. In either event, the perchlorate of the iron(III) complex was precipitated by adding dilute perchloric acid. A solution of the iron(III) complex was prepared by dissolving the perchlorate in concentrated perchloric or sulfuric acid and was stored in a refrigerator. It was found that the solutions in the concentrated acids were relatively stable, while solutions in dilute acid decomposed fairly rapidly.

Several of the iron(III) complexes were prepared by both methods of oxidation and yielded kinetic results which were identical within the experimental error.

Ferrous perchlorate (G. Frederick Smith) was purified by recrystallization from perchloric acid.

Perchloric acid (Baker Analyzed Reagent) and sulfuric acid (Baker and Adamson) were used without further purification.

Triply-distilled water was used in preparing the solutions for the kinetic measurements.

Apparatus.—The reactions were followed using the rapid-mixing and flow apparatus described by Sutin and Gordon.² Instead of using a gravity drive to mix the reactants, a constant speed motor with suitable gearing was adapted to this purpose.

Procedure.—The solutions of the perchlorates of the iron(III) complexes in either concentrated sulfuric or perchloric acid were examined spectrophotometrically using a Beckman DU instrument. These solutions then were standardized by reducing the iron(III) complex to the iron(II) complex with hydroxylamine, adding excess ligand and adjusting to pH 5 with sodium acetate. Alcohol was added if it was necessary to prevent the precipitation of the perchlorate of the iron(II) complex. The concentration of the iron(II) complex was determined spectrophotometrically using published values⁵⁻¹⁰ of the extinction coefficients.

The solutions of the iron(III) complexes in the concentrated acids were diluted by the required amount immedi-

ately before use in the kinetic measurements. Even so, it was found that with some of the compounds extensive decomposition took place during the time required to perform a series of runs. This was apparent from the fact that the maximum deflection obtained on the recording instrument decreased in a series of runs in which the ferrous ions were present in excess. Using these maximum deflections and the time from dilution of the solution of the iron(III) complex, it was possible to extrapolate back to zero time by assuming a first order decomposition of the complex.^{11,12} The decomposition of the iron(III) complexes was generally of the order of 5–10% during a series of six runs except in the case of 2,2',2''-tripyridine where as much as 60% decomposition took place. The correctness of the assumption of first order decomposition was demonstrated by the fact that the same half-life was observed for the decomposition regardless of the initial concentration of the iron(III) complex. The decomposition of both the iron(III) and the iron(II) complexes was found to be negligible during a particular run.

The procedure employed in the kinetic measurements was the same as that described by Sutin and Gordon.² In all reactions, one reactant was always present in at least two-fold excess. In most runs, ferrous ions were in excess. It was shown that the same second order rate constant was obtained if, instead, the iron(III) complex was present in excess. This provided a useful check on the concentration estimations.

Results

Spectrophotometric Measurements.—Table I lists the determined wave lengths of maximum absorption of the iron(III) complexes in concentrated sulfuric acid and the molar extinction coefficients at these wave lengths. It was found that the position of the maximum shifted about 5 μ to longer wave lengths on going from concentrated sulfuric to concentrated perchloric acid, but this shift was not accompanied by any significant change in the molar extinction coefficient. These results cannot be compared with data in

TABLE I
ABSORPTION SPECTRA OF SUBSTITUTED 1,10-PHENANTHROLINE, 2,2'-DIPYRIDINE AND 2,2,2''-TRIPYRIDINE COMPLEXES OF IRON(II) AND IRON(III)

Ligand	Wave length of maximum absorption, $m\mu$		Molar extinction coefficient, $cm.^2 \text{ mole}^{-1}$	
	Iron (III) complex in concd. H_2SO_4	Iron (II) complex in concd. water	Iron (III) complex in concd. H_2SO_4	Iron (II) complex in water
1,10-Phenanthroline	602	510 ^{a,b}	870	11,100
5-Methyl-1,10-phenanthroline	597	516 ^{a,b}	770	11,500
5-Nitro-1,10-phenanthroline	590	510 ^{a,b}	950	11,500
5-Chloro-1,10-phenanthroline	595	512 ^{a,b}	760	11,700
5-Phenyl-1,10-phenanthroline	599	515 ^a	780	11,000
5,6-Dimethyl-1,10-phenanthroline	600	512 ^d	780	12,400
4,7-Diphenyl-1,10-phenanthroline	628	533 ^e	2870	22,400
3,4,7,8-Tetramethyl-1,10-phenanthroline	670	500 ^d	1590	13,800
2,2'-Dipyridine	617	522 ^b	320	8,650
4,4'-Dimethyl-2,2'-dipyridine	591	529 ^c	390	8,470
2,2',2''-Tripyridine	702	552 ^f	740	12,500

^a Ref. 5. ^b Ref. 6. ^c Ref. 7. ^d Ref. 8. ^e Ref. 9. ^f Ref. 10.

(11) T. S. Lee, I. M. Kolthoff and D. L. Leussing, *J. Am. Chem. Soc.*, **70**, 3596 (1948).

(12) J. E. Dickens, F. Basolo and H. M. Neumann, *ibid.*, **79**, 1286 (1957).

(4) R. J. P. Williams, *J. Chem. Soc.*, 2015 (1958).

(5) W. W. Brandt and D. K. Gullstrom, *J. Am. Chem. Soc.*, **74**, 3532 (1952).

(6) M. L. Moss, M. G. Mellon and G. F. Smith, *Ind. Eng. Chem., Anal. Ed.*, **14**, 931 (1942).

(7) F. W. Cagle and G. F. Smith, *J. Am. Chem. Soc.*, **69**, 1860 (1947).

(8) W. W. Brandt and G. F. Smith, *Anal. Chem.*, **21**, 1313 (1949).

(9) G. F. Smith, W. H. McCurdy and H. Diehl, *Analyst*, **77**, 418 (1952).

(10) D. H. Wilkins and G. F. Smith, *Anal. Chem. Acta*, **9**, 338 (1953).

TABLE II
SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF IRON(II) IONS BY VARIOUS IRON(III) COMPLEXES AT 25.0°

Iron(III) complex	E^0 of complex, volt ^a	pK_a of ligand	$k(0.5F \text{ HClO}_4)$, $F^{-1} \text{ sec.}^{-1}$	$k(0.5F \text{ H}_2\text{SO}_4)$, $F^{-1} \text{ sec.}^{-1}$	$k(\text{H}_2\text{SO}_4)$ / $k(\text{HClO}_4)$
Tris-(1,10-phenanthroline)-iron(III)	1.06 ^b	4.86 ^c	3.7×10^{17}	3.0×10^8	8.1
Tris-(5-methyl-1,10-phenanthroline)-iron(III)	1.02 ^b	5.23 ^c	2.0×10^{17}	1.5×10^8	7.5
Tris-(5-nitro-1,10-phenanthroline)-iron(III)	1.25 ^b	3.57 ^c	1.1×10^{16}
Tris-(5-chloro-1,10-phenanthroline)-iron(III)	1.12 ^c	4.26 ^c	2.1×10^{16}	1.5×10^8	7.1
Tris-(5-phenyl-1,10-phenanthroline)-iron(III)	1.08 ^c	4.72 ^d	3.2×10^8	..
Tris-(5,6-dimethyl-1,10-phenanthroline)-iron(III)	0.97 ^d	7.8×10^8	6.9×10^8	8.8
Tris-(4,7-diphenyl-1,10-phenanthroline)-iron(III)	1.24 ^e	4.84 ^e	$(3.3 \times 10^4)^m$..
Tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)-iron(III)	0.81 ^f	6.31 ^f	1.9×10^8	..
Tris-(2,2'-dipyridine)-iron(III)	0.97 ^g	4.34 ^g	2.7×10^4	2.2×10^8	8.2
Tris-(4,4'-dimethyl-2,2'-dipyridine) iron(III)	0.95 ^g	6.0×10^2	5.9×10^8	9.8
Bis-(2,2',2''-tripyrindine)-iron(III)	0.93 ^h	5.04 ^h	8.5×10^4	7.4×10^8	8.7

^a The formal oxidation potentials of the complexes are in 1F H₂SO₄. ^b G. F. Smith and F. P. Richter, *Ind. Eng. Chem., Anal. Ed.*, **16**, 580 (1944). ^c G. F. Smith and D. K. Gullstrom, *J. Am. Chem. Soc.*, **74**, 3532 (1952). ^d G. F. Smith and W. W. Brandt, *Anal. Chem.*, **21**, 948 (1949). ^e Ref. 3. ^f Ref. 8. ^g G. F. Smith Chemical Co., Columbus, Ohio, Catalogue, January, 1960, p. 97. ^h F. P. Dwyer and E. C. Gyrfas, *J. Am. Chem. Soc.*, **76**, 6321 (1954). ⁱ A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, **60**, 1546 (1956). ^j J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950). ^k P. Offenhardt, G. P. Haight and P. George, Paper #55, Division of Physical Chemistry, ACS meeting, New York, 1960. ^l Ref. 2. ^m This value is not reliable because of the insolubility of the ferrous complex.

the literature since previously-reported spectra were measured in dilute acids. For purposes of comparison with the iron(III) complexes, the literature values of the wave lengths of maximum absorption and the molar extinction coefficients of the corresponding iron(II) complexes are included in Table I. The absorption spectra of a number of these complexes have been discussed by Williams.¹³

Kinetic Measurements.—The reactions were all found to be first order with respect to each of the reactants. Plots of $\log [b(a-x)/a(b-x)]$ versus t gave straight lines, where a and b are the initial concentrations of the reactants and x the concentration of the product at time t . The second order rate constants calculated from the slopes of these plots were found to be independent of the initial concentrations of each of the reactants. In some of the slower reactions, large excesses of ferrous ions were used and the reactions then were treated as pseudo-first order with respect to the iron(III) complex. For each pair of reactants at least six series of runs were carried out in both 0.5F HClO₄ and 0.5F H₂SO₄, and the mean of the rate constants in each medium was calculated. All the kinetic measurements were carried out at 25.0 ± 0.1°. Individual determinations of the rate constants differed from the mean by less than 10%.

Table II shows the second order rate constants for the reactions investigated as well as the pK_a of the ligands and the formal oxidation potentials of the iron(II) complexes in 1F H₂SO₄.

Discussion

Relation of the Rate Constants to the Basicity of the Ligands.—In Fig. 1 the logarithms of the second order rate constants for the oxidation-reduction reactions involving the substituted phenanthrolines are plotted against the average basicity per nitrogen atom of the ligand molecule.¹⁴ There appears to be a tendency for the

rates determined in H₂SO₄ solution to lie along a straight line and those determined in HClO₄ to lie along another straight line. A straight line dependence is found for phenanthroline and its derivatives formed by substitution of nitro, chloro, phenyl and methyl groups in the 5 position. (In perchloric acid a result is not available for the tetramethyl and the phenyl compounds because of the insolubility of the perchlorate salts of the complexes; in sulfuric acid the rate of the nitro compound was too fast to measure.) The rate constants measured in sulfuric acid for the 2,2'-dipyridine, 2,2',2''-tripyrindine, 4,7-diphenyl- and 3,4,7,8-tetramethyl-1,10-phenanthroline complexes all lie below the upper line in Fig. 1 by about a factor of ten. Thus we see that the expected linear relationship is found for a group of compounds which have the same ring structures and are substituted in the 5 position. It is interesting to note that Brandt and Wright¹⁴ found that both 2,2'-dipyridine and 2,2',2''-tripyrindine lay well below the straight line obtained by plotting the logarithm of the first order rate constant for the dissociation of the unsubstituted and 5-substituted phenanthroline complexes of iron(II) against the average basicity per nitrogen atom of the ligand molecule. However, Brandt and Wright used a value for the pK_a of 2,2',2''-tripyrindine considerably larger than the value reported in Table I.

Relation of the Rate Constants to the Standard Free Energy Changes of the Reactions.—Since the rates of oxidation-reduction reactions may be related to their standard free energy changes,^{2,15,16} we have plotted in Fig. 2 the free energies of activation against the standard free energy changes of the reactions involving the substituted phenanthrolines. The standard free energy change is calculated by combining the formal oxidation potential of the ferrous ion with that of the particular iron(II) complex being considered. Since the oxidation-reduction potentials of most of the complexes have been measured in sulfuric acid solution with the

(13) R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

(14) W. W. Brandt and J. P. Wright, *J. Am. Chem. Soc.*, **76**, 3082 (1954).

(15) D. H. Irvine, *J. Chem. Soc.*, 2977 (1959).

(16) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).

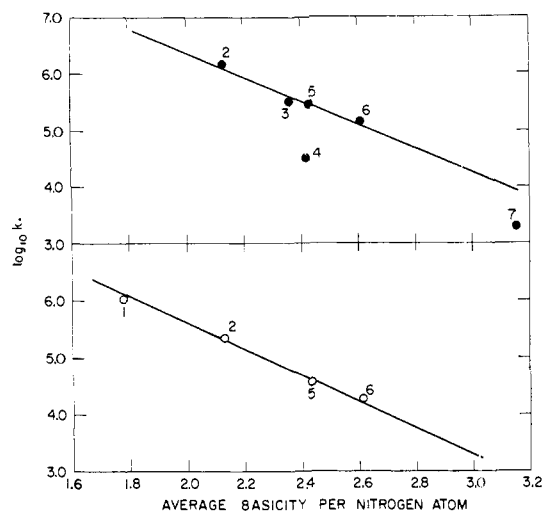


Fig. 1.—Relation between the logarithm of the second order rate constant and the average basicity per nitrogen atom of the ligand molecule; O, in $0.5F$ $HClO_4$, and ● in $0.5F$ H_2SO_4 : 1, tris-(5-nitro-1,10-phenanthroline)-iron(III); 2, tris-(5-chloro-1,10-phenanthroline)-iron(III); 3, tris-(5-phenyl-1,10-phenanthroline)-iron(III); 4, tris-(4,7-diphenyl-1,10-phenanthroline)-iron(III); 5, tris-(1,10-phenanthroline)-iron(III); 6, tris-(5-methyl-1,10-phenanthroline)-iron(III); 7, tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)-iron(III).

concentration of the acid in the range 1.0–3.0 M , we have used the formal oxidation potentials in H_2SO_4 of both the iron(II) complexes and the ferrous ion in estimating the value of ΔG^0 in $0.5F$ H_2SO_4 . The formal oxidation potential of the ferrous ion is 0.69 v. in $1F$ H_2SO_4 .¹³ For reasons of solubility, the oxidation–reduction potentials of the complexes have not been measured in perchloric acid solutions, so we have used the formal oxidation potentials of the iron(II) complexes in $1F$ H_2SO_4 to estimate the value of ΔG^0 in $0.5F$ $HClO_4$. However, the formal oxidation potential of the ferrous–ferric couple has been determined in $1.0F$ $HClO_4$ and has a value of 0.74 v.¹⁷

It will be seen from Fig. 2 that when the free energies of activation are plotted against the standard free energy changes of the reactions, most of the points again lie on two straight lines of identical slope, one line corresponding to the reactions carried out in H_2SO_4 and the other to those carried out in $HClO_4$. The intercepts of these lines differ by 0.5 kcal. mole⁻¹. If the oxidation–reduction potentials of the complexes were known in perchloric acid, then more realistic values of the standard free energy changes of the reactions in $0.5F$ $HClO_4$ could be calculated. It might then be found that the intercepts of the perchloric and sulfuric acid lines are identical. However, part of the Fe^{2+} ions exist as $FeSO_4$ and $FeHSO_4^+$ ions in sulfuric acid,¹⁸ and it may be that these species react more rapidly with the iron(III) complexes than free ferrous ions do.

The linear relationship between ΔG^* and ΔG^0 for a series of similar electron transfer reactions is

(17) W. C. Schumb, M. S. Sherrill and S. B. Sweetser, *J. Am. Chem. Soc.*, **59**, 2360 (1937).

(18) J. Beukenkamp and K. D. Herrington, *ibid.*, **82**, 3022 (1960).

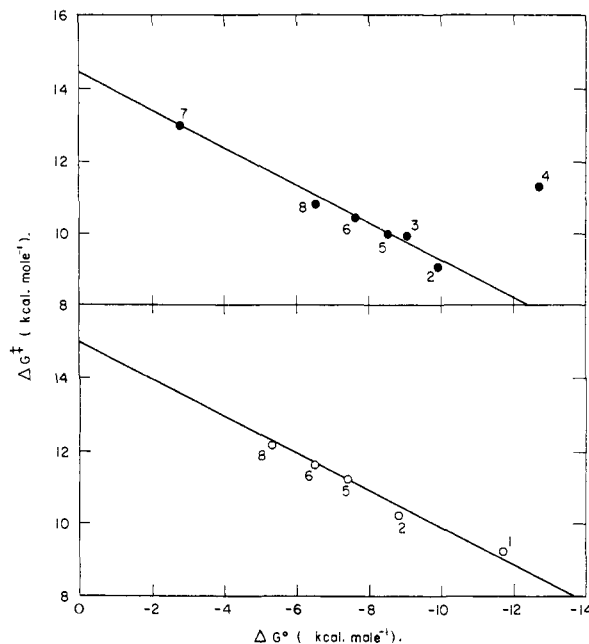


Fig. 2.—Relation between the free energy of activation and the standard free energy change of the reaction, O, in $0.5F$ $HClO_4$ and ●, in $0.5F$ H_2SO_4 . 1, tris-(5-nitro-1,10-phenanthroline)-iron(III); 2, tris-(5-chloro-1,10-phenanthroline)-iron(III); 3, tris-(5-phenyl-1,10-phenanthroline)-iron(III); 4, tris-(4,7-diphenyl-1,10-phenanthroline)-iron(III); 5, tris-(1,10-phenanthroline)-iron(III); 6, tris-(5-methyl-1,10-phenanthroline)-iron(III); 7, tris-(3,4,7,8-tetramethyl-1,10-phenanthroline)-iron(III); 8, tris-(5,6-dimethyl-1,10-phenanthroline)-iron(III).

expected from the Marcus theory of these reactions.¹⁶ This theory also predicts¹⁹ that the slope of the straight line obtained should be 0.5, and the fact that the observed slope is a significant confirmation of this prediction.

The rate constants measured in sulfuric acid for the 2,2'-dipyridine and 2,2',2''-tripyridine complexes lie below the lines, while the 4,4'-dimethyl-2,2'-dipyridine and 4,7-diphenyl-1,10-phenanthroline complexes lie above the lines. As in the earlier comparison, the anomalous behavior of the dipyridine and tripyridine complexes may be due to the fact that their structures differ considerably from those of the phenanthroline complexes. It is possible that the 4,7-diphenyl-1,10-phenanthroline complex reacts more slowly with ferrous ions than expected because the bulky phenyl groups introduce steric effects by blocking some of the possible directions of approach of the ferrous ion. However, the experimental data on this reaction are not reliable because of the extreme insolubility of the tris-(4,7-diphenyl-1,10-phenanthroline)-iron(II) compound. Moreover, Smith and Banick³ report that the formal oxidation potential of the 4,7-diphenyl-1,10-phenanthroline complex is anomalous with regard to the general relationship they found between E^0 and pK_a of the ligand. From this general relationship, they deduce that the true value should be 1.09 v. instead of 1.24 v. If 1.09 v. is indeed the correct value, then the 4,7-diphenyl-1,10-phenanthroline complex

(19) R. A. Marcus, *J. Chem. Phys.*, **26**, 872 (1957).

lies much closer to the straight line than indicated in Fig. 2. Since the unsubstituted, the 5-substituted, the 5,6-dimethyl- and the 3,4,7,8-tetramethyl phenanthroline complexes all lie on the straight lines, there appears to be no specific steric effect present in the reactions of the 1,10-phenanthroline complexes of iron(III) with ferrous ions. It thus seems reasonable to suppose that the electron-transfer between the iron(III) complex and the ferrous ion does not take place in an activated complex in which the ferrous ion is located on the periph-

ery of a phenanthroline group, but instead it may be necessary for the ferrous ion to penetrate the space between the phenanthroline groups. This conclusion is supported by the fact that the entropy of activation of the reaction between ferrous ions and the tris-(1,10-phenanthroline)-iron(III) ion is considerably more negative than that of other iron(II)-iron(III) reactions.²

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[CONTRIBUTION FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL OF CANADA, OTTAWA, CANADA]

The Temperature Dependence of the Solvent Isotope Effect¹

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Rate data for the hydrolysis of isopropyl bromide in deuterium oxide have been determined over a temperature of 35 to 80°. By comparison with earlier data for hydrolysis in water, it was shown that the solvent isotope effect (k_{D_2O}/k_{H_2O}) decreased with increasing temperature more rapidly than the solvent isotope effect for relaxation processes in bulk solvent. While this conclusion may be general for the hydrolysis of halides, it will not hold for the sulfonates where very much smaller values of $d(k_{D_2O}/k_{H_2O})/dT$ are found. The sources of the solvent isotope effect for hydrolysis are examined. The results are shown to be consistent with the hypothesis that the major contribution to the observed characteristic differences resides in the relative structural stability of the initial state solvation shells.

In a recent paper³ evidence was given to show how the "solvent isotope effect" obtained from the ratio of the rates of hydrolysis in light and heavy water (k_{D_2O}/k_{H_2O}) might appreciably alter with temperature over the available experimental range. This conclusion was at variance with our earlier claim⁴ that the temperature dependence of this ratio was small or zero and that of Swain and Bader⁵ who concluded that the change in the solvent isotope effect with temperature was rapid at lower temperatures (say below 18°) but became small or zero above this temperature. Our earlier inference was based on limited data for the hydrolysis of the benzenesulfonates and methanesulfonates and is still essentially correct for those molecules which interact only weakly with water in the initial state. However, some doubts were raised as to the generality of this conclusion when the similarity was noted between the trend in the values of the k_{D_2O}/k_{H_2O} ratio for a series of halides reacting over a wide range of temperature and the corresponding variation in the values for the relative fluidity⁶ (ϕ_{D_2O}/ϕ_{H_2O}) and time of dielectric relaxation⁷ (τ_{D_2O}/τ_{H_2O}) for bulk H₂O and D₂O over the same range. But, while it may be quite reasonable to relate the temperature dependence observed in the ratios ϕ_{D_2O}/ϕ_{H_2O} and τ_{D_2O}/τ_{H_2O} to corresponding relative changes in structural stability of the bulk solvent (see below), a similar postulate for the temperature dependence of $k_{D_2O}/$

k_{H_2O} from data for a series of halides was less obvious. Thus, because of the possibility of specific differences in both the initial⁸ and transition states,⁹ our conclusions concerning the temperature dependence of k_{D_2O}/k_{H_2O} was less convincing in our recent paper³ than if it had been based on data for a single compound obtained over a range of temperature. This has now been done and we report here the results of such a study for the hydrolysis of isopropyl bromide.

Isopropyl bromide was chosen as a suitable test compound, not only because other evidence suggested that in hydrolysis nucleophilic interaction was reduced compared to the primary halides but also because of convenient rates of hydrolysis in the accessible temperature range. Rate data for the hydrolysis of isopropyl bromide in H₂O over the necessary range of temperature were already known¹⁰ and could be expressed within experimental error by the equation (T in °K.)

$$\log k = -9306.912/T - 27.37569 \log T + 93.53701 \quad (1)$$

Corresponding data for hydrolysis in heavy water were obtained by the same conductometric techniques which have been described previously.¹¹⁻¹³ Temperature control and measurement as well as methods of calculation were uniform with the earlier work.

The isopropyl bromide used was a fractionated sample of Eastman White Label (b.p. 59-60° and $n_{D_2O}^{20}$ 1.4251) and was kept in the dark under refrigeration during the course of the investigation.

(1) Issued as N.R.C. No. 6209.

(2) National Research Council of Canada Postdoctoral Fellow.

(3) P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **37**, 1491 (1959).

(4) R. E. Robertson and P. M. Laughton, *ibid.*, **35**, 1319 (1957).

(5) C. G. Swain and R. F. W. Bader, *Tetrahedron*, **10**, 182 (1960). (The authors are grateful for receiving a preprint of this paper.)

(6) R. C. Harday and R. L. Cottingham, *J. Research Natl. Bur. Standards*, **42**, 573 (1949).

(7) C. H. Collie, F. B. Hasted and D. M. Ritson, *Proc. Phys. Soc.*, **60**, 145 (1948).

(8) T. S. Morrison and N. B. Johnstone, *J. Chem. Soc.*, 3441 (1954).

(9) R. E. Robertson, R. L. Heppollette and J. M. W. Scott, *Can. J. Chem.*, **37**, 803 (1959).

(10) R. L. Heppollette, R. E. Robertson and J. M. W. Scott, unpublished work.

(11) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953).

(12) R. E. Robertson, *ibid.*, **33**, 1336 (1955).

(13) K. T. Leffek, J. A. Llewellyn and R. E. Robertson, *J. Am. Chem. Soc.*, **82**, 6315 (1960).