[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

A Spectrophotometric Study of the Hydrolysis of Iron(III) Ion. III. Heats and Entropies of Hydrolysis

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The hydrolysis of iron(III) ion has been studied over a range of ionic strengths up to 1.00 at the temperatures 18, 25 and 32°. Free energy, heat and entropy changes are calculated for the reactions $Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+$ and $2FeOH^{2+} \rightleftarrows Fe(OH)_2Fe^{4+}$. Over the range investigated, increases in temperature or decreases in ionic strength shift the first hydrolysis equilibrium to the right, and the dimerization equilibrium to the left. A negative value of $\Delta S°$ found for the dimerization reaction is discussed in qualitative terms. For comparative purposes thermodynamic quantities are calculated for the derived reactions $2Fe^{3+} + 2H_2O \rightleftarrows Fe(OH)_2Fe^{4+} + 2H^+$ and $Fe^{3+} + OH^- \rightleftarrows FeOH^{2+}$.

In part II[1] the hydrolysis of iron(III) ion was studied at 25° and the experimental results were interpreted in terms of the reactions

$$Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+ \qquad (1)$$

and

$$2FeOH^{2+} \rightleftarrows Fe(OH)_2Fe^{4+} \qquad (2)$$

Equilibrium quotients for these reactions were reported as a function of ionic strength.

An extension of this work to cover a temperature range has now made possible the calculation of heat and entropy changes for reactions 1 and 2, and for derived reactions 3 and 4.

$$2Fe^{3+} + 2H_2O \rightleftarrows Fe(OH)_2Fe^{4+} + 2H^+ \qquad (3)$$

$$Fe^{3+} + OH^- \rightleftarrows FeOH^{2+} \qquad (4)$$

Experimental

Procedure.—The preparation of materials and standard solutions, and the spectrophotometric technique have been previously described.[1] The thermostat on the spectrophotometer was adjusted to allow solutions to be held at either 18 ± 0.1, 25 ± 0.1, or 32 ± 0.1°. A stock 0.0997 *M* iron(III) perchlorate solution, 0.1263 *M* in perchloric acid, was used for the preparation of all other iron(III) solutions. Ionic strengths were adjusted by the addition of the required amount of sodium perchlorate.

Temperature Dependence of the First Hydrolysis.—Four 9.97×10^{-5} *M* iron(III) perchlorate solutions were prepared, each 1.113×10^{-2} *M* in perchloric acid, and one at each of the ionic strengths 1.17×10^{-2}, 2.17×10^{-2}, 3.17×10^{-2} and 1.00. The absorbance of each solution at 340 mμ was measured at 18, 25 and 32°. Values for k_1, the equilibrium quotient for reaction 1, were calculated from equation 2 of part II,[1] with $e_1 = 925$. As before, preliminary values for k_1 were first estimated making the approximations $[H^+] = h_0$ and $d_h = d$. This procedure permitted calculation of the fractions of iron(III) hydrolyzed, α, and hence the corrected acidities, $[H^+]$, and the corrected absorbances, d_h. Final values for k_1 at the various temperatures and ionic strengths are presented in Table I.

TABLE I

EQUILIBRIUM QUOTIENTS FOR REACTION 1 AT 18, 25 AND 32°

$\mu \times 10^2$	1.17	2.17	3.17	100
$k_1 \times 10^3$, 18°	2.83	2.51	2.35	1.10
$k_1 \times 10^3$, 25°	4.25	3.80	3.53	1.64
$k_1 \times 10^3$, 32°	6.43	5.65	5.25	2.47

At each temperature the results for the three lowest ionic strengths were used to extrapolate k_1 to zero ionic strength, using the equation

$$\log k_1 = \log k_1^0 - 4A\mu^{1/2}/(1 + 2.4\mu^{1/2}) \qquad (5)$$

with A equal to 0.503, 0.509 and 0.516 for the respective temperatures 18, 25 and 32°.[2,3] The results of the extrapolation were: $T = 18°$, $k_1^0 = 4.2 \times 10^{-3}$; $T = 25°$, $k_1^0 = 6.4 \times 10^{-3}$; $T = 32°$, $k_1^0 = 9.5 \times 10^{-3}$. The value for 25° is in satisfactory agreement with our previous work.[1,4] In a plot of $\log k_1^0$ against $1/T°A$ the points fall on a straight line within the experimental limits of error, showing that $\Delta H°$ is sensibly constant over the temperature range investigated. The least squares slope gives $\Delta H° = 10.4$ kcal. An uncertainty of ±0.2 kcal. is estimated. Equation 6

$$\Delta S = (\Delta H - \Delta F)/T°A \qquad (6)$$

with $\Delta H° = 10.4 \pm 0.2$ kcal. and $\Delta F° = 2.96 \pm 0.04$ kcal.,[5] gives $\Delta S° = 25.0 \pm 0.7$ e.u. When the $\log k_1$ values corresponding to unit ionic strength are plotted against $1/T°A$, a straight line is again obtained within the limits of experimental error, and the least squares slope gives $\Delta H = 10.2$ kcal.[6] The estimated uncertainty is ± 0.3 kcal. From equation 6, with $\Delta H = 10.2 \pm 0.3$ kcal. and $\Delta F = 3.80 \pm 0.04$ kcal., $\Delta S = 21.6 \pm 1.0$ e.u.

Temperature Dependence of the Dimerization.—Four 9.97×10^{-3} *M* iron(III) perchlorate solutions were prepared, each 4.12×10^{-2} *M* in perchloric acid, and one at each of the ionic strengths 0.103, 0.203, 0.303 and 1.00. The absorbance of each solution at 340 mμ was measured at 18, 25 and 32°. Before calculating values for k_d, the equilibrium quotient for reaction 2, it was necessary to have knowledge of k_1 at each temperature and ionic strength. For $\mu = 1.00$, the k_1 values quoted above were used. For each of the three other ionic strengths, k_1 was calculated from equation 5, with the appropriate values for k_1^0 and A, also given above. For each solution, the corrected acidity, $[H^+]$, and the corrected absorbance, d_h, were estimated by taking the first hydrolysis into account in accordance with the method of part II.[1] Values of k_d were then calculated from equation 10 of part II, with $e_1 = 925$ and $e_d = 3.0 \times 10^3$. The results are shown in Table II.

TABLE II

EQUILIBRIUM QUOTIENTS FOR REACTION 2 AT 18, 25 AND 32°

$\mu \times 10$	1.03	2.03	3.03	10.0
k_d, 18°	270	420	500	980
k_d, 25°	220	320	390	730
k_d, 32°	170	240	300	510

Following the procedure of part II,[1] $\log k_d^0$ values for each temperature were obtained by plotting $\log k_d - (8A\mu^{1/2})/(1 + 2.1\mu^{1/2})$ against μ, and extrapolating to $\mu = 0$.[2] The dimerization quotients obtained, with estimated uncertainties, were $T = 18°$, $k_d^0 = 47 \pm 16$; $T = 25°$, $k_d^0 = 36 \pm 12$; $T = 32°$, $k_d^0 = 26 \pm 9$. The value for 25° agrees satisfactorily with our previous result.[1] Most of the estimated

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(1) R. M. Milburn and W. C. Vosburgh, THIS JOURNAL, **77**, 1352 (1955).

(2) The values of A were interpolated from the values of G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, *ibid.*, **65**, 1765 (1943).

(3) The empirical constant 2.4 previously has been used for the representation of k_1 values at 25°.[1]

(4) T. H. Siddall and W. C. Vosburgh, THIS JOURNAL, **73**, 4270 (1951).

(5) All free energy values used in this paper for calculation of entropy changes have been taken from equilibrium quotients reported in part II.[1]

(6) Throughout this paper, the superscript zeros are limited to symbols for true thermodynamic properties at $\mu = 0$.

TABLE III

EQUILIBRIUM QUOTIENTS AND FREE ENERGY, HEAT AND ENTROPY CHANGES FOR HYDROLYSIS REACTIONS OF IRON(III) ION AT 25°[a]

Reaction		μ	k	ΔF	ΔH	ΔS
$Fe^{3+} + H_2O \rightleftarrows FeOH^{2+} + H^+$	(1)	0	$6.7(\pm 0.4) \times 10^{-3}$	2.96 ± 0.04	10.4 ± 0.2	25.0 ± 0.7
		1	$1.65(\pm 0.10) \times 10^{-3}$	3.80 ± 0.04	10.2 ± 0.3	21 ± 1
$2FeOH^{2+} \rightleftarrows Fe(OH)_2Fe^{4+}$	(2)	0	$30(\pm 10)$	-2.0 ± 0.2	-7.3 ± 1.0	-18 ± 4
		1	$700(\pm 200)$	-3.9 ± 0.2	-8.2 ± 1.0	-14 ± 4
$2Fe^{3+} + 2H_2O \rightleftarrows Fe(OH)_2Fe^{4+} + 2H^+$	(3)	0	$1.4(\pm 0.4) \times 10^{-3}$	3.9 ± 0.2	13.5 ± 1.0	32 ± 4
		1	$1.9(\pm 0.6) \times 10^{-3}$	3.7 ± 0.2	12.2 ± 1.2	28 ± 5

[a] Equilibrium quotients and thermodynamic quantities for reaction 3 were calculated from the corresponding values for reactions 1 and 2. The equilibrium quotients for reactions 1 and 2 are those given in part II.[1] ΔF values, in kcal. mole^{-1}, were calculated from the corresponding equilibrium quotients; ΔH values, also in kcal. mole^{-1}, were calculated from the temperature dependent measurements of the present study; and ΔS values, in entropy units, were obtained from the corresponding values of ΔF and ΔH, using equation 6.

uncertainty in the absolute magnitude of each k_d^0 value arises from a corresponding uncertainty in e_d at 340 mμ. The assumption of various values of e_d within the limits of error given in part II[1] has little effect on the trend of k_d^0 with temperature. This fact lends confidence to a calculation of ΔH^0. A plot of log k_d^0 against $1/T^0 A$ gives a straight line within the experimental limits of error. From the least squares slope, $\Delta H^0 = -7.3$ kcal. An uncertainty of ±1.0 kcal. is estimated. From equation 6, with $\Delta H^0 = -7.3 \pm 1.0$ kcal. and $\Delta F^0 = -1.99 \pm 0.20$ kcal., $\Delta S^0 = -18 \pm 4$ e.u. At $\mu = 1.00$, log k_d against $1/T^0 A$ gives a straight line within experimental limits of error, and the least-squares slope gives $\Delta H = -8.2$ kcal. An uncertainty of ±1.0 kcal. is estimated. From $\Delta F = -3.89 \pm 0.20$ kcal., $\Delta S = -14 \pm 4$ e.u.

In Table III is given a summary of the thermodynamic data obtained. Figure 1 illustrates the plots of log k against $1/T^0 A$ used for the determination of the heats of reaction.

Discussion

The first stage in the hydrolysis of iron(III) ion may be represented by either equation 1 or 4. In part II[1] a comparison was given of our equilibrium quotients for reaction 1 at 25° with other values reported for this temperature.[7]

Heat and entropy changes for reaction 1, reported by Rabinowitch and Stockmayer,[8] were calculated both from their temperature dependent measurements and from the k_1^0 values of Bray and Hershey.[9] Rabinowitch and Stockmayer utilized 0.1 M iron(III) perchlorate solutions, 0.50 M in perchloric acid and with an ionic strength of 1.10. Their determination was based on the assumption that reaction 1 alone would be important. Neglect of dimerization may explain the discrepancy between their ΔH value (12.3 ± 1.0 kcal., $\mu = 1.10$) and ours (10.2 ± 0.3 kcal., $\mu = 1.00$).[10] Bray and Hershey deduced k_1^0 at 25° from the experimental work of Popoff, Fleharty and Hanson,[11a] and k_1^0 at 35° from the work of Fleharty.[12] At each temperature sufficiently dilute iron(III) solutions were used to avoid serious error from polynuclear species. A recalculation of ΔH^0, using the k_1^0 values and limits of error reported by Bray and Hershey, gives 12.6 ± 3.0 kcal. The possible margin of error places this value in satisfactory agreement with our work ($\Delta H^\circ = 10.4 \pm 0.2$ kcal.).

Rabinowitch and Stockmayer,[8] using their own ΔH value, calculated ΔS^0 for reaction 1 both from the k_1^0 value at 25° reported by Bray and Hershey,[9] and from the k_1^0 value at 25° given by Lamb and Jacques.[12] The first calculation gave $\Delta S^0 = 31$ e.u.; the second gave $\Delta S^0 = 30$ e.u. For reaction 1 we obtain $\Delta S^0 = 25\ (\pm 0.7)$ e.u.; the differences between this result and those reported by Rabinowitch and Stockmayer can be largely attributed to the different values of ΔH used.

Several papers[13] have made use of the k_1 values 1.18×10^{-3} at 15° and $\mu = 0.5$ obtained by Connick, *et al.*,[13b,c] 1.9×10^{-3} at 25° and $\mu = 0.5$ obtained by Bray and Hershey,[9] and 3.2×10^{-3} at 35° and $\mu = 0.5$ calculated by extrapolation[13b,c] of the 15 and 25° values. Postmus and King[13d] have observed that the ΔH and ΔS values for 25° calculable from the above values of k_1 are 8.8 kcal. and 17 e.u., respectively. Published details concerning the measurements of Connick, *et al.*, at 15° do not permit an estimate of the uncertainties in the above values of ΔH and ΔS.

From our thermodynamic data for reaction 1, together with that accepted for the reaction $H^+ + OH^- \rightleftarrows H_2O$,[14] a recalculation for reaction 4 gave $\Delta F^0 = -16.1$ kcal., $\Delta H^0 = -3.0$ kcal., and $\Delta S^0 = 44$ e.u.[15] The heat changes for reactions 2 and 4 have the same sign and favor the forward reactions. But the entropy changes have opposite signs; for reaction 2, $\Delta S^0 = -18\ (\pm 4)$ e.u., while for reaction 4, $\Delta S^0 = +44\ (\pm 1)$ e.u.

Entropy changes for reactions such as 4, involving the combination of oppositely charged ions in aqueous solution, are generally positive. The

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[7] The value $k_1 = 1.6 \times 10^{-3}$ at 25° and $\mu = 0.5$ reported by A. S. Wilson and H. Taube, THIS JOURNAL, **74**, 3509 (1952), was omitted from part II.[1]

[8] E. Rabinowitch and W. H. Stockmayer, *ibid.*, **64**, 335 (1942).

[9] W. C. Bray and A. V. Hershey, *ibid.*, **56**, 1889 (1934).

[10] A calculation shows the importance of dimerization in the solutions of Rabinowitch and Stockmayer. Using our values of k_1 and k_d for unit ionic strength, it was estimated that the ratio of concentration of dimer to $FeOH^{2+}$ ion would have been 0.24 at 25°, and would have increased by about 0.03 for each 10° rise. If the dimer absorbs significantly at 400 mμ, we can explain a high value for ΔH obtained by Rabinowitch and Stockmayer; if $e_d \gg e_1$ at this wave length, they should have obtained 12.4 kcal. (compare with 12.3 ± 1 kcal. found) instead of 10.2 kcal. as measured in the present investigation. Although other polynuclear species, *e.g.*, the $Fe(OH)Fe^{5+}$ ion, would possibly exist in solutions of such high total iron(III) concentration, they have not been taken into account in this calculation.

[11] (a) S. Popoff, V. B. Fleharty and E. L. Hanson, THIS JOURNAL, **53**, 1643 (1931); (b) V. B. Fleharty, *ibid.*, **55**, 2646 (1933).

[12] A. B. Lamb and A. G. Jacques, *ibid.*, **60**, 1215 (1938).

[13] (a) L. G. Hepler, J. W. Kury and Z. Z. Hugus, Jr., *J. Phys. Chem.*, **58**, 26 (1954); (b) R. E. Connick and M. Tsao, THIS JOURNAL, **76**, 5311 (1954); (c) R. E. Connick, L. G. Hepler, Z. Z. Hugus, Jr., J. W. Kury, W. M. Latimer and M. Tsao, *ibid.*, **78**, 1827 (1956); (d) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

[14] Values of ΔF°, ΔH° and ΔS° for this reaction were calculated from the data of Table II, p. 39, W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., second edition, 1952.

[15] These values for reaction 4 may be compared with those given by Rabinowitch and Stockmayer[8]: $\Delta F^\circ = -16.0$ kcal., $\Delta H^\circ = -1.2$ kcal., and $\Delta S^\circ = 50$ e.u.

positive values are usually attributed to the water molecules having greater freedom in the field of the complex ion or molecule than in the fields of the separate ions.[16-19] The magnitudes of the entropy changes have been found to depend both on the charges and sizes of the reactant ions and of the complexes, and on the number of water molecules replaced upon complex formation from the first coördinated spheres of the reactant ions.[16-18] Calculated values of ΔS for complex formation, using the empirical relation proposed by Cobble,[17] are in reasonable agreement with experiment for reactions of the type $Fe^{3+} + X^- \rightleftarrows FeX^{2+}$. Application of this relation to reaction 4 gives $\Delta S = +34$ e.u.,[20] compared with the experimental values of +44 e.u. obtained in the present paper, and +50 e.u. found by Rabinowitch and Stockmayer.[8]

The dimerization of iron(III) may be represented by either equations 2 or 3. For 25° and an ionic strength of 3, Hedström[21] reports an equilibrium quotient for reaction 3 of 1.22 (± 0.10) $\times 10^{-3}$; our work[1] corresponds to 2.6 (± 0.9) $\times 10^{-3}$; while Mulay and Selwood[22] report a value of 7.3×10^{-3}.[23] Because of approximations made, Mulay and Selwood consider their value to be in satisfactory agreement with Hedström. Mulay and Selwood have made an approximate determination of the temperature dependence of the quotient, from which they compute ΔH for reaction 3 to be ≈ 9.8 kcal., with $\mu = 3$. At $\mu = 1$ we find $\Delta H = 12.2$ (± 1.2); at $\mu = 0$ we find $\Delta H^0 = 13.5$ (± 1.0). The agreement between the three values is not unreasonable.

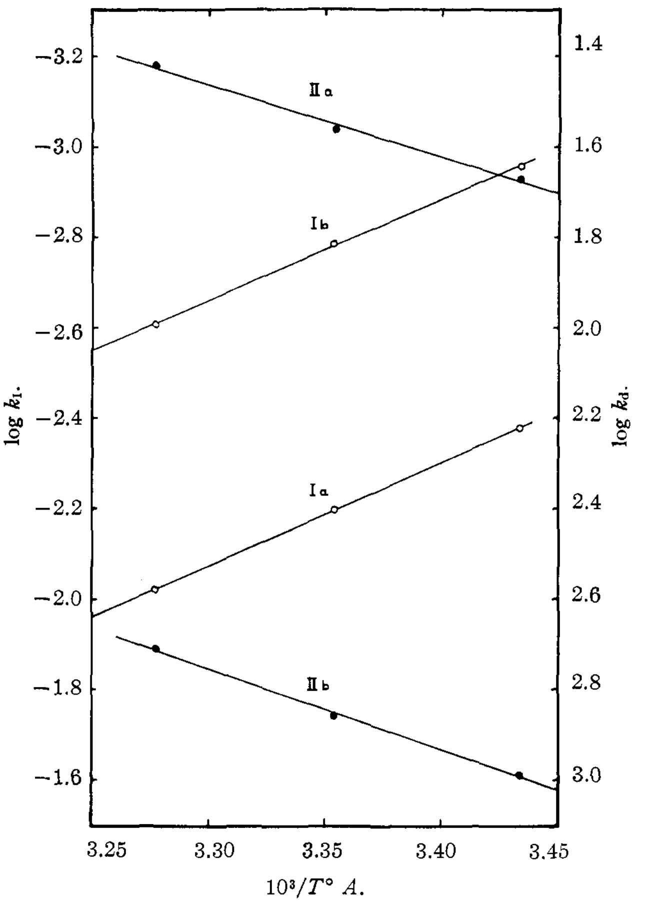

Fig. 1.—Determination of ΔH for the first hydrolysis and dimerization reactions from plots of log k against $1/T°A$: curve Ia, log $k_1°$; curve Ib, log k_1 for $\mu = 1.00$; curve IIa, log $k_d°$; curve *IIb*, log k_d for $\mu = 1.00$.

Dimerization reactions have been reported[24] for a number of other ions of the type MOH^{+n}. Heats and entropies have been measured for the dimerization of $CeOH^{3+}$ ion by Hardwick and Robertson,[25] and for the dimerization of the $ScOH^{2+}$ ion by Kilpatrick and Pokras.[26] The latter workers found that ΔH and ΔS varied greatly over the temperature range 10 to 40°; this lack of constancy does not permit a comparison of their results for scandium with ours for iron(III). Kilpatrick and Pokras have suggested that the trends found in their values may be a consequence of neglect of equilibria involving higher polymers. Hardwick and Robertson[25] explained their experimental work on the basis that the $CeOH^{3+}$ ion dimerizes, and have assumed the reaction to be

$$2CeOH^{3+} \rightleftarrows CeOCe^{6+} + H_2O \qquad (7)$$

The possibility that dimerization proceeds according to reaction 8 was not considered.

$$2CeOH^{3+} \rightleftarrows Ce(OH)_2Ce^{6+} \qquad (8)$$

Whichever formulation describes the actual reaction, Hardwick and Robertson's measured values of ΔH and ΔS would be equally valid. For an ionic strength of 2, they reported $\Delta H = -16 \pm 1$ kcal., and $\Delta S = -48.3$ e.u. Both the heat and entropy changes are negative, as they are for reaction 2 in the present work.

It is generally assumed that a rapid and reversible dimerization of MOH^{+n} ions will result in the formation of $M(OH)_2M^{+2n}$ ions. The general reaction may be represented by

$$2[M(OH)(H_2O)_y]^{+n}_{aq} \rightleftarrows [M(OH)_2M(H_2O)_{(2y-z)}]^{+2n}_{aq} + zH_2O$$

where y and $y - z/2$ indicate the number of water molecules in the first hydration sphere of a single

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(16) W. M. Latimer and W. L. Jolly, THIS JOURNAL, **75**, 1548, 4147 (1953).

(17) J. W. Cobble, *J. Chem. Phys.*, **21**, 1446 (1953).

(18) R. J. P. Williams, *J. Phys. Chem.*, **58**, 121 (1954).

(19) E. L. King, *J. Chem. Educ.*, **30**, 71 (1953).

(20) It was assumed that the OH^- ion takes the place of one water molecule in the first hydration sphere of the Fe^{3+} ion; see Cobble.[17] The ionic radius of the OH^- ion was taken as 1.53 Å. (see A. F. Wells, "Structural Inorganic Chemistry," Clarendon Press, second edition, 1950, p. 70), and the ionic radius of the Fe^{3+} ion as 0.67 Å. (see R. W. G. Wyckoff, "Crystal Structures," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1951, Chap. 3, table p. 15).

(21) B. O. A. Hedström, *Arkiv Kemi*, **6**, 1 (1953).

(22) L. N. Mulay and P. W. Selwood, THIS JOURNAL, **77**, 2693 (1955).

(23) In table 9 of a stimulating review by L. Pokras, *J. Chem. Educ.*, **33**, 223 (1956), Hedström's value for this quotient should read 1.22×10^{-3} instead of 12.2×10^{-3}, and Milburn and Vosburgh's value at $\mu = 3.00$ should read 2.6×10^{-3} instead of 26×10^{-3}.

(24) Refer to table 11, L. Pokras, *J. Chem. Educ.*, **33**, 223 (1956); see also reference 25 below.

(25) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951).

(26) M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, **101**, 39 (1954).

metal atom in the monomer and dimer, respectively. Although z will be positive, and may generally equal +2, the measured entropy changes for dimerization of both the $FeOH^{2+}$ and $CeOH^{3+}$ ions are negative. The loss in independent motion that the monomeric ions experience upon combination would contribute toward negative entropy changes. It is also likely that a dimeric ion of charge $+2n$ would exert a greater restrictive influence over surrounding water molecules than would two monomeric ions of charge $+n$. As yet no satisfactory approach has been made toward the quantitative estimation of entropies for these dimerization reactions. Before this problem can be attacked profitably, entropies for other dimerization reactions should be obtained.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

An Investigation of the Species Existing in Nitric Acid Solutions Containing Cerium(III) and Cerium(IV)[1]

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Extraction data and electromotive force measurements are interpreted as indicating the existence of cerium(IV)–cerium(IV) and cerium(IV)–cerium(III) polymers in 5.5 *f* nitric acid solutions. If the polymers are assumed to be dimers, the association constants for the reactions $2Ce^4 = (Ce^4)_2$, $Ce^4 + Ce^3 = Ce^4Ce^3$ in this medium are 17 ± 2 and 2.0 ± 0.7 at 30.0 ± 0.03° where total concentration of monomer and of dimer are used in the equilibrium expressions. Contradictory reports in the literature are reconciled by the existence of these dimeric species. The cerium(IV) species extracted by ether is shown to contain no ionizable hydrogen.

Introduction

The fact that ceric cerium forms complex ions with various anions has been known for some time.[2] The formal electrode potentials vary from −1.2 to −1.7 depending upon whether the solution contains hydrochloric, sulfuric, nitric or perchloric acids. Cerium(IV) migrates to the anode in 1 *f*[3a, 3b] sulfuric acid and in 6 *f* nitric acid; but it travels to the cathode in 1.8 *f* sulfuric acid and does not migrate in 2 *f* nitric acid. The formation constants for the various sulfate complexes of cerium(IV) have been measured.[4] More recently the ability of cerium(III) to form complex ions has been verified.[5] Several independent methods have been employed[6] to show the existence of cerium(IV) polymers in perchloric acid solutions even at high acidities. In spite of the existence of cerium(IV) complexes with nitrate, Noyes and Garner[7] present evidence that the cerium(IV)–cerium(III) electrode potential in nitric acid is essentially independent of nitric acid concentration. Yost, *et al.*,[2] postulate mixed hydroxide–nitrate complexes to account for these results. Cerium(IV) in nitric acid can be extracted by a number of solvents.[8] Wylie[8b] studied the nature of the compound extracted into diethyl ether and concluded that it has the formula $H_2Ce(NO_3)_6$.

The present investigation was initiated to study the nitrate complexes of cerium(IV) by an extraction procedure. In the course of the work, it was found that much of the cerium(IV) existed as polymers even in 5.5 *f* HNO_3 and the emphasis of the study was reoriented toward an investigation of these polymers.

Experimental

Materials.—Matheson, Coleman and Bell Practical Grade diisopropyl ether was purified by washing with alkaline permanganate, water, ceric nitrate in nitric acid and finally several more times with water. The ether, to which some hydroquinone had been added, was dried over $CaCl_2$ and $MgSO_4$, and then with some low-melting Na-amalgam (108 g. Hg/100 g. Na). The mixture was refluxed under nitrogen for two hours and then distilled in a nitrogen atmosphere at the rate of 400–500 ml./hr. The uncorrected boiling point of the material was 66° with a boiling range of 1°. The purified ether was made 2×10^{-5} *f* in hydroquinone to inhibit peroxide formation.[9] Ether purified in this fashion and stored for months in the dark before use contained no detectable amounts of peroxide, when tested either with a sulfuric acid solution of Ti(IV)[10] or with a 2% solution of KI and starch.

The stock solution of $LiNO_3$ (Mallinckrodt Analytical Reagent) was analyzed by converting an aliquot portion to Li_2SO_4 which was ignited and weighed as such.

The HNO_3 solutions were prepared by diluting either fresh, unopened Baker Analyzed Reagent concentrated nitric acid or a concentrated HNO_3 solution brought rapidly to a boil to expel nitrogen oxides and then cooled. The

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(1) This work was presented at the 130th meeting of the American Chemical Society at Atlantic City and is abstracted from a thesis submitted by B. D. Blaustein to the Faculty of Philosophy of The Johns Hopkins University in conformity with the requirements for the degree of Doctor of Philosophy.

(2) See, for example, D. M. Yost, H. Russell and C. S. Garner, "The Rare Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 61.

(3) (a) Concentration will be expressed in formality, *f*, formula weights per liter of solution. (b) V. J. Linnenbom and A. C. Wahl, THIS JOURNAL, **71**, 2589 (1949).

(4) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

(5) (a) R. E. Connick and S. W. Mayer, THIS JOURNAL, **73**, 1176 (1951); (b) T. W. Newton and G. M. Arcand, *ibid.*, **75**, 2449 (1953).

(6) (a) L. J. Heidt and M. E. Smith, *ibid.*, **70**, 2476 (1948); (b) E. L. King and M. L. Pandow, *ibid.*, **74**, 1966 (1952); (c) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951); (d) K. A. Kraus, R. W. Holmberg and F. Nelson, Atomic Energy Commission Report AECD2070; (e) K. A. Kraus and F. Nelson AECD1888.

(7) A. A. Noyes and C. S. Garner, THIS JOURNAL, **58**, 1265 (1936).

(8) (a) L. Imre, *Z. anorg. allgem. Chem.*, **164**, 214 (1927); (b) A. W. Wylie, *J. Chem. Soc.*, 1474 (1951); (c) J. C. Warf, THIS JOURNAL, **71**, 3257 (1949); (d) J. C. Warf, U. S. Patent 2,523,892.

(9) R. J. Myers, D. E. Metzler and E. H. Swift, THIS JOURNAL, **72**, 3767 (1950).

(10) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," 3rd ed., Vol. II, D. Van Nostrand and Co., Inc., New York, N. Y., 1949, p. 882.