Inorganica Chimica Acta, 143 (1988) 277–280

Thermodynamic Parameters of Complexation of Lanthanoid(III) with Ascorbic Acid

YUKO HASEGAWA, TETSUKO SUGAWARA

Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162, Japan

and GREGORY R. CHOPPIN

Department of Chemistry, The Florida State University, Tallahassee, Fla. 32306, U.S.A.

(Received August 10, 1987)

Abstract

The thermodynamic parameters of formation of the 1:1 complex between trivalent lanthanide cations and ascorbic acid have been determined for 0.1 M and 2.0 M ionic strengths at 25 °C by potentiometric and calorimetric titration. Comparison of these values with data for other organic ligands indicates that in the complex $LnAsc^{2+}$ the ascorbate functions as an inner sphere monodentate ligand more similar to benzoate than to kojate.

Introduction

The thermodynamic parameters of complexation of lanthanide cations with a number of organic carboxylic acid ligands have been measured. For the monocarboxylate ligands, correlation of $\log \beta_{101}$ (*i.e.*, the stability constant for the formation of the 1:1 complex) with the pK_a values of the ligand acids confirmed the primarily electrostatic nature of the lanthanide–carboxylate binding. The positive values of the enthalpy and entropy changes, ΔH_{101}, and ΔS_{101}, reflect the significant dehydration attendant to the complexation [1]. For dicarboxylic acid ligands, the size of the chelate ring was shown to be a major factor in the strength of the complexation [2].

Less attention has been given to complexation reactions involving ligands with acidic hydroxyl groups. Squaric [3] and croconic [4] acids, involving ortho hydroxyl groups, have been found to form chelates as do kojic acid [5] and tropolone [6], involving ortho carbonyl and hydroxyl groups. In this paper we report the results of a study of complexation between lanthanides and ascorbic acid. Ascorbic acid has two hydroxyl groups and one carbonyl group on consecutive carbon atoms.

Experimental

The preparation of reagents and the procedures were the same as described in previous publications [7, 8]. The solutions were adjusted to 2.0 M or 0.10 M ionic strength with sodium perchlorate. The dissociation constant (K_a) and the enthalpy change of protonation (ΔH_{011}) of ascorbic acid were measured by potentiometric and calorimetric titration of half-neutralized ascorbate solution by perchloric acid. The stability constants and the complexation heats were determined by titrating metal(III) solutions with the ascorbate buffer solution in similar fashion to the titrations used to determine the pK_a and the ΔH_{011}. The net heat of complexation was calculated by subtracting the heat of dilution and the heat of protonation from the experimental heat changes.

Since ascorbic acid is a reductant, the acid may be decomposed by oxygen gas dissolved in the solution. Therefore, initially the stability constants were determined under nitrogen gas. However, no difference was found in these values with those determined in the presence of air so the effect of oxygen is apparently negligible under our experimental conditions. However, when ascorbate solution was added to the europium(III) solution, even under nitrogen gas, the color of the solution turned to yellow. The color change may be due to the decomposition of ascorbate ions, and/or reduction of Eu(III) to Eu(II), which is consistent with our inability to obtain reliable values of europium(III) complexation.

Results

The pK_{a1} of ascorbic acid in 2.0 M ionic strength was determined to be 4.11; the pK_{a2} was not determined. Values of 3.96 and 10.35 were reported [9] in 0.10 M KNO_3 solution for pK_{a1} and pK_{a2}, respectively.

The protonation heat was calculated as follows: for each point of the calorimetric titration of half-neutralized ascorbate solution with perchloric acid, the mole concentration of ascorbic acid in the cup was calculated using the mass balance and the K_{a1} value. The correlation of the observed heat and the number of moles of ascorbic acid (HA) in the calorimeter cup for a typical run is shown in Fig. 1.

0020-1693/88/$3.50

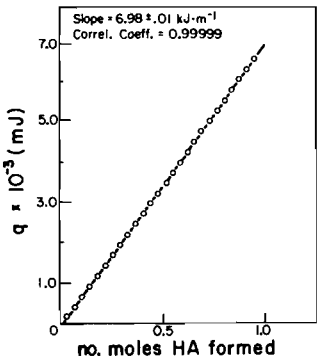

Fig. 1. Plot of the heat evolved and the concentration of undissociated ascorbic acid in a titration by 9.17×10^{-2} M $HClO_4$ at 25.0 °C and 2.0 ($NaClO_4$) ionic strength. The total ascorbic (HAs + As^-) concentration was 0.123 M.

The slope of this curve, determined by a least squares analysis, gave the heat evolved on the formation of one mole of ascorbic acid. This protonation heat, ΔH_{011}, was -6.98 ± 0.005 kJ/mol, at 25.0 °C in 2.0 M sodium perchlorate solution. The entropy change on protonation, ΔS_{011}, was calculated to be 55.2 J/(mol K). From a similar experiment in 0.1 M sodium perchlorate solution, 4.02 and −6.8 (kJ/mol) were obtained as the pK_a and the ΔH_{011} values, respectively. The concentration of the background salt does not seem to have a large effect on the protonation of the ascorbate anion.

The stability constants were determined by treating the data obtained from the pH titrations by the Bjerrum formation function. The complexation reaction

$$Ln^{3+} + nA^- = LnA_n^{3-n} \quad (1)$$

has a stability constant defined by

$$\beta_{10n} = \frac{[LnA_n^{3-n}]}{[Ln^{3+}][A^-]^n} \quad (2)$$

The heat evolved per one mole of complex formed is defined as the complexation heat. This was calculated from each point in the calorimetric titrations of the lanthanide solutions with the half-neutralized ascorbate solutions. The amount of the complex formed at each titrant addition was calculated from the equations for the mass balance, the stability constant and the pK_a. The observed heat was corrected for the dilution and protonation heats. From the net heat and the number of moles of complex formed, the molar heat of complex formation was calculated.

As a check on the stability constants obtained by potentiometry, separate calculations of the calorimetric data were made in which the stability constants were varied until values were obtained for which the calculated molar enthalpy changes at each point agreed over the widest range of experimental data. These stability constants agreed well with those obtained by potentiometry. However, the values of β_{102} did not seem to be sensitive to the ΔH_{101}; e.g.,

TABLE I. Sample Set of Titration Data in 2.0 M ($NaClO_4$) at 25 °C

Ho(III) solution ($V_{(initial)}$ = 40.0 ml; $C_{(initial)} = 8.69 \times 10^{-3}$ M; $pH_{(initial)}$ = 4.07$_3$)		Ascorbate solution ($C_{(initial)}$ = 0.157M)	
Volume of titrant (ml)	pH	[A^-] (M) (×10^3)	$\bar{n}$
(a) Potentiometric data			
0.5	4.03(6)	0.8	0.021
1.0	4.03(4)	1.59	0.041
1.5	4.03(3)	2.35	0.062
2.0	4.03(1)	3.09	0.083
2.5	4.03(1)	3.82	0.104
3.0	4.03(1)	4.53	0.124
3.5	4.03(1)	5.23	0.145
4.0	4.03(1)	5.91	0.165
4.5	4.03(3)	6.60	0.182
5.0	4.03(3)	7.25	0.202
5.5	4.03(4)	7.92	0.218
6.0	4.03(4)	8.55	0.238
6.5	4.03(4)	9.16	0.258
7.0	4.03(6)	9.80	0.272
7.5	4.03(6)	10.4	0.291
8.0	4.03(6)	11.0	0.311
8.5	4.03(6)	11.5	0.330
9.0	4.03(8)	12.1	0.343
9.5	4.03(8)	12.7	0.361
10.0	4.03(8)	13.2	0.380

$\log \beta_{101} = 1.41$; $\log \beta_{102} = 2.3$

Ho(III) solution ($V_{(initial)}$ = 50.0 ml; $C_{(initial)} = 9.38 \times 10^{-3}$ M; $pH_{(initial)}$ = 4.2)		Ascorbate solution ($C_{(initial)}$ = 0.184 M)	
Volume of titrant (ml)	Observed heat evolved (mJ)	[A^-] (×10^3)	ΔH_{101} (kJ mol^{-1})
(b) Calorimetric data			
2.5	251.8	3.60	5.97
3.0	301.0	4.29	5.77
3.5	344.3	4.97	5.75
4.0	384.5	5.64	5.79
4.5	430.1	6.30	5.77
5.0	477.4	6.95	5.70
5.5	511.8	7.59	5.73
6.0	556.8	8.23	5.71
6.5	595.8	8.85	5.71
7.0	640.8	9.47	5.67
		Average =	5.76

TABLE II. Thermodynamic Parameters for the Formation of 1:1 Lanthanide(III)–Ascorbate Complexes at 25.0 °C

Metal	$\log \beta_{101}$	$-\Delta G_{101}$ (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔS_{101} (J K^{-1} m^{-1})
(a) 2.0 M ($NaClO_4$)				
La	1.41	8.07	3.1(5)	37.7
Pr	1.48	8.43	3.4(0)	39.7
Nd	1.54	8.81	2.7(1)	38.7
Sm	1.68	9.59	4.1(0)	45.9
Gd	1.52	8.66	3.7(0)	41.5
Tb	1.52	8.66	6.0(0)	49.2
Dy	1.45	8.26	4.6(0)	43.2
Ho	1.41	8.07	5.8(0)	46.5
Er	1.45	8.26	8.0(0)	54.6
Tm	1.41	8.07	6.8(0)	49.9
Yb	1.41	8.07	7.8(0)	53.3
Lu	1.32	7.54	5.4(0)	43.4
(b) 0.1 M ($NaClO_4$)				
Pr	1.6(0)	9.1	3.2	41
Tb	1.7(1)	9.7	3.8	45
Dy	1.3(0)	7.4	5.5	43
Er	1.4(6)	8.3	8.0	55
Yb	1.8(0)	10.3	4.0	48
Lu	1.7(8)	10.2	4.4	49

increasing the values of the second stability constant by a factor of ten did not influence the values of ΔH_{101}. This reflected that the values of $\bar{n}$ in the calorimetric experiments were relatively low ($\leqslant 0.4$). Even for the pH titrations, since the β_{102} values had such large uncertainties, no values are reported.

Table I gives a sample set of titration data from which the thermodynamic parameters of the complexation were calculated.

Table II lists the thermodynamic values on the complexation in 2.0 M ($NaClO_4$) solution and in 0.1 M ($NaClO_4$) solution.

Discussion

Berger has studied the ^{13}C NMR shifts of ascorbic acid as a function of pH [10]. The shifts showed that the ionization of the protons produced the ascorbate anions with the structures shown in Fig. 2. For the mononegative anion, metal ions could form monodentate complexes or, by involving the hydroxyl group, bidentate chelate structures. The α-hydroxy carboxylates such as glycolate and lactate form chelated complexes. Moreover, lanthanides react with kojate [5], tropolonate [6], and acetylacetonate [12] which have carbonyl and acidic hydroxyl groups to form 5 and 6 membered chelate rings.

Figure 3 is a plot of $\log \beta_{101}$ for Sm(III) complexation as a function of the ligand pK_a. The complexes

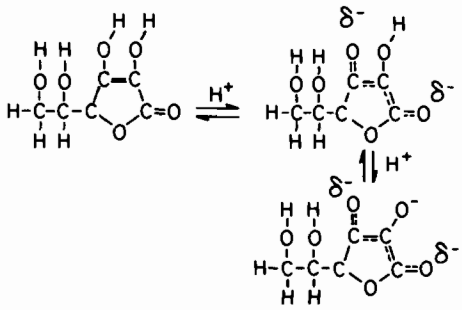

Fig. 2. Formal structures of ascorbate anion species.

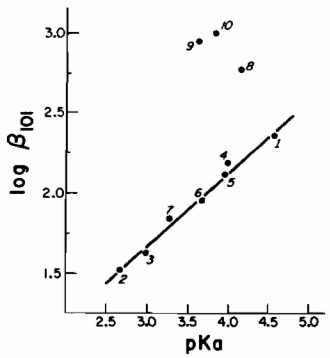

Fig. 3. Correlation of $\log \beta_{101}$ with ligand pK_a for Sm(III) with acetate (1), iodoacetate (2), chloroacetate (3), benzoate (4), 4-fluorobenzoate (5), 3-fluorobenzoate (6), 3-nitrobenzoate (7), squarate (8), glycolate (9) and α-hydroxyisobutyrate (10).

of acetates and benzoates are monodentate and fall on a common line. The chelated complexes do not correlate with this line as they are more stable. The agreement of the ascorbate complexation stability constant with the correlation line for the monodentate ligands is strong evidence that the ascorbate complexes are not chelates.

The thermodynamic parameters also provide evidence of the nature of the ascorbate complex. Figure 4 shows the trends in enthalpy and entropy ($T\Delta S$) changes for formation of some lanthanide complexes (ΔG values are not plotted as their correlation is seen in Fig. 3). In general, we see that the monodentate complexes (e.g., with benzoate) have more positive values of ΔH_{101} and $T\Delta S_{101}$ compared to the chelated systems (e.g., with kojate). Again, the ascorbate complexation agrees with this correlation.

As can be seen from these data, ascorbic acid is a relatively weak complexant when it is in the form of the uninegative anion. This is reflected in the monodentate nature of the complexes formed. At sufficiently high pH values, the dinegative anion forms and should form much stronger complexes with a chelate structure. This is consistent with the reported stability constants with Fe^{2+} of $\log \beta = 0.21$ for

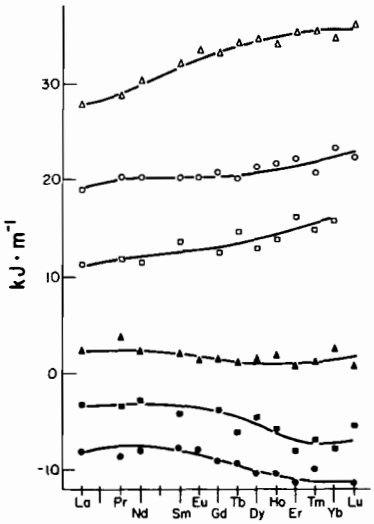

Fig. 4. Variation of the complexation enthalpies (solid symbols and entropies (open symbols) with lanthanide atomic number for benzoate (●, ○), kojate (▲, △), and ascorbate (■, □).

formation of $FeAsc^{1+}$ and of $\log \beta = 1.99$ for $FeAsc^{0}$. For the pH values in biological systems, from our lanthanide data we would expect that ascorbate, as a uninegative anion would form weak, monodentate complexes with cations such as Mg^{2+} and Ca^{2+}. Values for formation of $CaAsc^{1+}$ are reported to be $\log \beta = 0.2$ in $I = 0.16$ M and 0.03 in $I = 3.0$ M [9], which are consistent with monodentate complexation.

Acknowledgement

This research was supported partially at The Florida State University by a contract with the U.S.D.O.E.-O.B.E.S., Division of Chemical Sciences, and also supported partially by a Grant-in-Aid for Scientific Research No. 56540351 from the Ministry of Education, Science and Culture, Japan.

References

1 G. R. Choppin, *Pure Appl. Chem., 27,* 23 (1971).
2 G. R. Choppin, A. Dadgar and E. N. Rizkalla, *Inorg. Chem., 25,* 3581 (1986).
3 E. Orebaugh and G. R. Choppin, *J. Coord. Chem., 5,* 123 (1976).
4 G. R. Choppin and E. Orebaugh, *Inorg. Chem., 17,* 2300 (1978).
5 R. Stampfli and G. R. Choppin, *J. Coord. Chem., 1,* 173 (1971).
6 D. L. Campbell and T. Moeller, *J. Inorg. Nucl. Chem., 32,* 945 (1970).
7 G. R. Choppin, P. A. Bertrand, Y. Hasegawa and E. N. Rizkalla, *Inorg. Chem., 21,* 3722 (1982).
8 H. Yoneda, G. R. Choppin, J. L. Bear and J. V. Quagliano, *Inorg. Chem., 3,* 1642 (1964).
9 A. E. Martell and R. M. Smith (eds.), 'Critical Stability Constants', Vol. 3, Plenum, New York, 1977.
10 S. Berger, *Tetrahedron, 33,* 1587 (1977).
11 G. R. Choppin and H. G. Friedman, *Inorg. Chem., 5,* 1599 (1966).
12 A. Dadgar and G. R. Choppin, *J. Coord. Chem., 1,* 179 (1972).