Physico-Chemical Studies on the Composition and Stability of Copper Chelates of 2-Hydroxystearic and 2-Hydroxydocosanoic Acids

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Abstract

The complex formation of copper (II) with 2-hydroxystearic and 2-hydroxydocosanoic acids has been investigated at pH 8.0 in a medium of *m*-xylene-ethanol (75:25 v/v). The formation of only one complex metal: ligand (1:2) is detected by three independent methods, viz. Job's method of continuous variation, conductometric titration and chemical analysis of the isolated complexes. The logarithm of the formation constants (log K) as calculated by the method of Turner and Anderson are 6.30 and 5.73 and the free energy change of combination are, −8.590 kcal and −7.814 kcal respectively. A chelate structure for both the complexes, in which the ligand molecules act as a bidentate chelating species involving the weakly coordinating hydroxyl group in bond formation has been suggested by analogy with the copper derivatives of amino acids.

Introduction

The 2-hydroxy acids are of great importance since they have valuable surface active properties and their derivatives are good lubricants for heavy-duty metals (1). The metal complexes of 2-hydroxy acids are of special interest in that the cadmium salts have been generally employed for stabilizing vinyl polymers (2), and lithium and magnesium chelates have been used to isolate 2-hydroxy acids from a mixture of acids having several polar substituents (3,4). Moreover, the reaction between cupric acetate and 2-hydroxy acids has been in practical use as a simple procedure for quantitative separation of 2-hydroxy acids from nonhydroxy acids (5,6). A few preliminary reports (7,8) and patent literature (9) also describe metal chelates of 2-hydroxy acids. In spite of the practical significance of the above reaction, very little attention has been given to study it systematically.

The present communication deals for the first time, with physico-chemical studies on the composition and stability of the copper chelates of 2-hydroxystearic and 2-hydroxydocosanoic acids.

Materials and Methods

Reagents

The 2-hydroxy acids were obtained as side products in the preparation of α,β-unsaturated acids by the procedure of Palameta and Prostenik (6) in which the separation of 2-hydroxy acids was effected through copper-chelate formation. To a mixture of α,β-unsaturated acids and 2-hydroxy acids in 95% ethanol, powdered cupric acetate was added in small portions until no more dissolved. Most of the solvent was removed under reduced pressure. The chelate precipitate was washed thoroughly with ether and acetic acid to remove excess of cupric acetate, filtered, washed with ether and dried.

The copper chelates on shaking with 1:1 aqueous hydrochloric acid followed by ether extraction and crystallization from ethanol furnished 2-hydroxystearic acid (I), (Found C, 72.5%; H, 12.7%; $C_{18}H_{36}O_3$ requires C, 72.0%; H, 12.0%), and 2-hydroxydocosanoic acid (II), (Found C, 74.6%; H, 12.5%; $C_{22}H_{44}O_3$ requires C, 74.1%; H, 12.4%). The purity of these acids was checked by TLC, the method is described elsewhere (10). From the R_f values it was judged that the 2-hydroxy acids were extremely pure ($R_f \times 100$ values of 2-hydroxystearic acid was 88 and 2-hydroxydocosanoic acid was 96, the solvent system being etherlight petroleum, 30:70 v/v).

Stock solutions of these acids were prepared in ethanol and *m*-xylene separately. Alcoholic solutions were used for conductometric titration and for the preparation of copper chelates and the *m*-xylene solutions for spectrophotometric studies. Cupric acetate was first dissolved in ethanol and for spectrophotometric studies, this solution was diluted with *m*-xylene to give a final composition of xylene-ethanol (75:25 v/v). Alcoholic potassium hydroxide was employed to adjust the pH (8.0) of the reaction mixture.

Copper chelates of both the acids were isolated by suitably mixing equimolar solutions of cupric acetate and the respective hydroxy acid so as to give metal-ligand ratio of 1:1 and 1:2. Both the complexes were obtained as pale blue precipitates, differing from copper derivatives of nonhydroxy acids which are deep blue precipitates. The chelates were centrifuged, decanted, washed twice with ethanol and dried to a constant weight in a vacuum desiccator. An accurately weighed amount of each complex was ignited at 700 C to 800 C to constant weight and weighed as CuO.

Apparatus

Conductometric titrations were carried out on Type 01/02 conductivity bridge with dip type cell. Optical density measurements at 600 to 750 mμ were made on a Unicam SP 600 spectrophotometer. Lambert-Beer's law was found to hold good through the whole range of cupric acetate concentrations (1.0×10^{-4}M to 22.5×10^{-4}M). All measurements were carried out at room temperature (25 C). The pH of the reaction mixture was measured on a Beckman automatic titrator unit.

Results and Discussion

Chemical analyses of copper chelates of acid (I) obtained by mixing separately the reactants in 1:1 and 1:2 ratios gives in both cases a value of 9.56% of copper. Assuming a 1:2 combination, the theoretical value of copper per 100 g of chelate would be 9.61 g. Similarly copper chelate of acid (II) contains 8.43 g of copper per 100 g of the chelate. If

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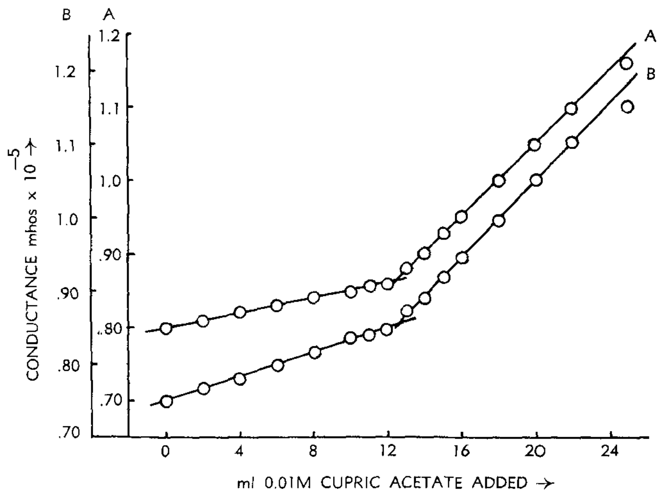
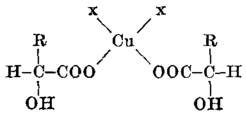


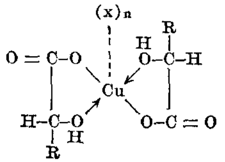
FIG. 1. Conductometric titrations of (A) 50 ml of 0.005 M 2-hydroxystearic acid against 0.01 M cupric acetate and (B) 50 ml of 0.005 M 2-hydroxydocosanoic acid against 0.01 M cupric acetate.

a 1:2 complex is assumed for the acid (II) also, the theoretical value would be 8.24%. Results of conductometric titrations of copper acetate-acid (I) and copper acetate-acid (II) are represented in Figure 1 (A and B respectively). Inflections are obtained when the metal and ligand are present in a 1:2 ratio. These results clearly indicate that 2-hydroxy acids form dicomplexes with cupric ion.

Job's method of continuous variation (11–13) has been employed to confirm the combining ratio obtained by above methods. Equimolar solutions [2.0 × 10^{-3}M of copper acetate and acid (I) and 2.5 × 10^{-3}M of copper acetate and acid (II)], were mixed and optical density measured at 675 mμ (absorption maximum). The results are depicted in Figures 2A and 3A where the difference in optical density (ΔOD) of the complex and pure copper acetate is plotted against the concentration of the reactants. Maxima are obtained at a mole fraction (copper) value of 0.334 with both acids and indicate 1:2 combinations. Thus a structure for dicomplex of cupric ion with 2-hydroxy acids can be represented as I or II



I



II

where R = $CH_3(CH_2)_{15}$ or $CH_3(CH_2)_{19}$ and x may be an anion (either CH_3COO or OH).

In order to calculate the stability constants, use has been made of the Turner and Anderson dilution method (13,14).

Complex formation proceeds by the pathway

$$nA + mB \rightleftharpoons A_nB_m \qquad [1]$$

in which A is a metallic ion and B an organic molecule or an anion. If a and b are the initial concentration of A and B and x is the equilibrium concentration of the complex, then equilibrium constant

$$K = \frac{x}{(a\text{-}nx)^n(b\text{-}mx)^m} \qquad [2]$$

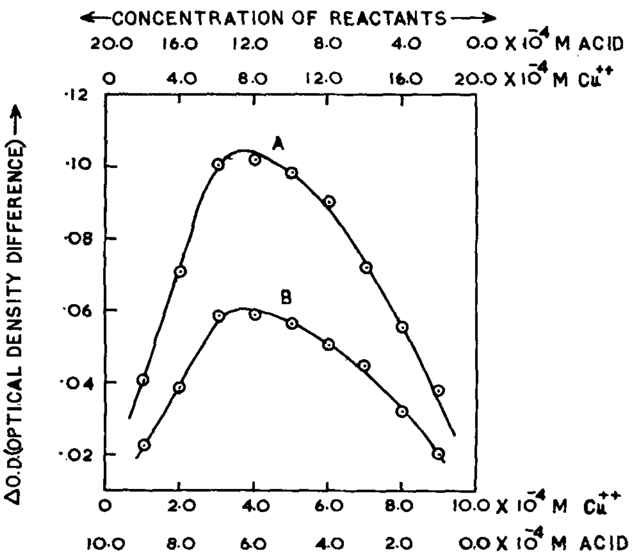


FIG. 2. Variation of Δ OD with varying concentration of cupric acetate and 2-hydroxystearic acid. Original concentration of reactants 2.0 × 10^{-3} M. Final concentration range (A) 2.0 × 10^{-4} M to 18.0 × 10^{-4} M (B) 1.0 × 10^{-4} M to 9.0 × 10^{-4} M. Upper scale for curve A and lower scale for curve B.

which for a dicomplex (where n = 1 and m = 2) becomes

$$K = \frac{x}{(a\text{-}x)(b\text{-}2x)^2} \qquad [3]$$

To determine the value of x, Job's method again is employed, but with different initial concentration of the reactants. Equimolar solutions of acid (I) and copper acetate (1.0 × 10^{-3}M) and acid (II) and copper acetate (1.25 × 10^{-3}M) were mixed and optical density measured at 675 mμ. The results are plotted in Figures 2B and 3B (dilution curves for acid (I) and acid (II) complexes respectively). From these dilution curves and the data of Figures 2A and 3A series of pairs of solutions could be selected with equal optical density (and thus essentially equal concentra-

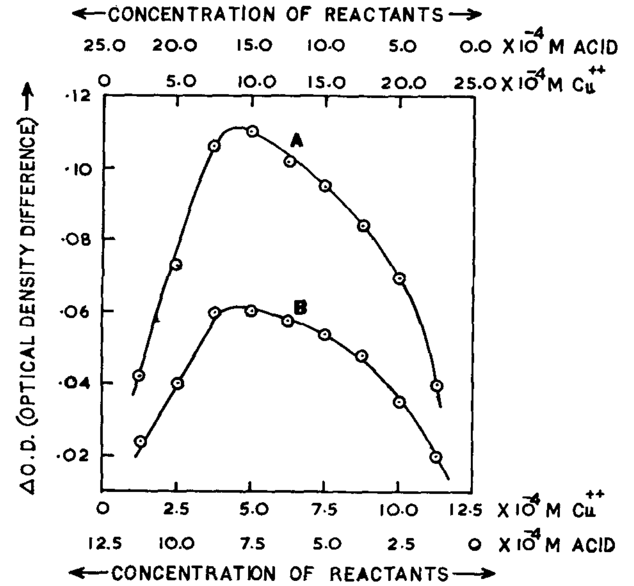


FIG. 3. Variation of Δ OD with varying concentration of cupric acetate and 2-hydroxydocosenoic acid. Original concentration of the reactants 2.5 × 10^{-3} M. Final concentration range (A) 2.5 × 10^{-4} M to 22.5 × 10^{-4} M (B) 1.25 × 10^{-4} M to 11.25 × 10^{-4} M. Upper scale for curve A and lower scale for curve B.

TABLE I
Binding Data Calculated From the Curves of Figures 2 and 3[a]

$a_1 \times 10^{-4}$M	$b_1 \times 10^{-4}$M	x $\times 10^{-4}$M	log K	$a_2 \times 10^{-4}$M	$b_2 \times 10^{-4}$M	x $\times 10^{-4}$M	log K
Copper chelates of 2-hydroxystearic acid							
16.40	3.60	0.923	6.30	6.00	4.00	0.923	6.60
2.60	17.40	2.83	6.10	2.70	7.30	1.83	......
Mean log K, 6.30 ± 0.30					—ΔF, 8.590 kcal		
Copper chelates of 2-hydroxydocosanoic acid							
22.00	3.00	0.426	5.63	8.25	4.25	0.426	5.67
2.50	22.50	2.17	5.90	3.25	9.25	2.17	......
Mean log K, 5.73 ± 0.17					—ΔF, 7.814 kcal		

[a] a_1, b_1, a_2 and b_2 (initial concentration of the reactants) were obtained from curve A and B of Figures 2 and 3. First and fourth rows represent the values obtained from right side of the peak and second and fifth rows represent the values obtained from the left side of the peak.

tion of the complex) but different concentration of reactants. If two concentrations $(a_1 + b_1)$ and $(a_2 + b_2)$ of the reactants have the same optical density, then the equilibrium constant (15)

$$K = \frac{x}{(a_1\text{-}x)(b_1\text{-}2x)^2} = \frac{x}{(a_2\text{-}x)(b_2\text{-}2x)^2} \qquad [4]$$

This equation could be solved for x, as follows

$$(a_2\text{-}x)(b_2^2\text{-}4b_2x + 4x^2) = (a_1\text{-}x)(b_1^2\text{-}4b_1x + 4x^2) \qquad [5]$$

On simplifying and rearranging the different terms in appropriate fashion, we get,

$$x^2\,[(4a_2+4b_2)-(4a_1+4b_1)] + x[(4a_1b_1+b_1^2)-(4a_2b_2+b_2^2)] = a_1b_1^2 - a_2b_2^2 \qquad [6]$$

and neglecting the first term of left hand side (since $x^2 << x$), the following equation is obtained.

$$x = \frac{a_1b_1^2\text{-}a_2b_2^2}{(4a_1b_1 + b_1^2)\text{-}(4a_2b_2 + b_2^2)} \qquad [7]$$

Thus knowing the value of x, at a known concentration of reactants, K could be calculated. In actual practice a line at optical density difference of 0.05 was drawn parallel to the concentration axis (not shown in Fig.) which intersects the curves A and B. A point corresponding to the intersection at curve A gives a_1 and b_1 on concentration axis, and on curve B gives a_2 and b_2 (on right side of the peak). Similarly another pair of a_1, b_1 and a_2, b_2 could be selected on left side of the peak and x may be calculated for each complex so also log K values. The results are shown in Table I.

The log K values thus calculated are 6.30 and 5.75 for copper complexes of acid (I) and acid (II) respectively and free energy change of combination are −8.590 kcal and −7.814 kcal respectively.

A comparison of the stabilities of Cu-citrate, Cu-tartrate, Cu-acid (I) and Cu-acid (II) complexes leads to the possible formula of the present Cu-2-hydroxy acid chelates. Structure (I) is analogous to the structure of Cu-citrate salt $[CuA_2(OH_2)]$ as proposed by Meites (16) on the basis of polarographic studies. This complex possesses an abnormally high degree of stability (log K, 19.3). On the other hand Cu-citrate (17) and Cu-tartrate (18) complexes in which the hydroxyl group of the respective acids is involved in bond formation, possess stability constants (log K values are 6.4 and 4.5 respectively), of the order comparable to the stabilities of the copper chelates of present 2-hydroxy acids. Thus the structure (I) which has been suggested simply on the basis of combining ratio of 1:2 appears improbable. Moreover, structure (I) is the structure of ordinary metal salts of fatty acids which are deep blue in color. On the basis of the unusual color of the present chelates (pale blue), the possibility of formation of these chelates as represented by structure (I) may be ruled out. Alternatively, it is assumed that the 2-hydroxy acids would function as bidentate ligands and both carboxyl and adjacent hydroxyl groups involve in bond formation for which a tentative structure (II) by analogy with copper chelates of amino acids can be presumed. Since the coordination number of copper (II) is 4, therefore, the value of n is zero.

The formation of chelate ring illustrated by structure (II) would require combination of metal ions with the relatively weak coordinating hydroxyl groups, therefore the copper chelates of 2-hydroxy acids should be considerably weaker than the analogous α-amino acid chelates. The copper chelates of alanine and its higher homologues possess very high degree of stability (19,20,21) as compared to 2-hydroxy acids (log K are shown in parenthesis).

Norvaline (15.28) > Norleucine (15.20) > α-alanine (14.82) > acid (I) (6.3) > acid (II) (5.73).

This is consistent with the present interpretation.

ACKNOWLEDGMENTS

K. T. Achaya, M. R. Subbaram and E. R. Saxena gave much helpful advice during the course of this work.

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[Received August 25, 1968]