CHALCONES AS INORGANIC ANALYTICAL REAGENTS

Part III. Spectrophotometric Study of the Germanium Complex with 2′, 3′, 4′-Trihydroxy Chalcone

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ABSTRACT

1·0–6·0 p.p.m. of germanium could be estimated spectrophotometrically with 2′, 3′, 4′-trihydroxy chalcone as reagent at pH 5·8–6·0. The complex was shown to contain three gram-moles of the reagent to one gram-atom of germanium both by Job's method of continuous variations and the slope ratio method of Harvey and Manning. The instability constant was determined by the method of Edmonds and Birnbaum and found to be $1 \cdot 670 \times 10^{-11}$ at 28° C. It is concluded that complex formation involved only the two ortho hydroxyls in each molecule of the reagent and the carbonyl group played no part.

INTRODUCTION

2′, 3′, 4′-Trihydroxy chalcone[1] gave an yellow precipitate with germanium. The precipitate dissolved in 50% alcohol to yield an orange-yellow to yellow-coloured solution. This reaction was found to be highly sensitive; the limits of identification and dilution being 0·625 γ and 1 : 80,000. Hence this colour reaction was investigated spectrophotometrically.

EXPERIMENTAL

Reagents

Chalcone solution.—2′, 3′, 4′-Trihydroxy chalcone (1·280 gm.) was weighed out accurately, dissolved in alcohol and the solution made up to 100 ml. with alcohol to yield a 0·05 M solution. Lower concentrations were prepared by diluting appropriate volumes with alcohol.

Germanium solution.—This solution was prepared as per the procedure of Beltz and Mellon.[2]

Germanium dioxide (0·6245 gm., Spec Pure; Johnson and Matthey) was weighed out accurately and fused with 3–4 gm. of A.R. sodium carbonate in a platinum crucible. The clear melt was dissolved in water and the excess carbonate was neutralised with dilute sulphuric acid. The solution was made up to 500 ml. with water to yield 0·0119 M solution. Lower concentrations of the solution were prepared by diluting appropriate volumes with water.

Buffer solution.—A buffer solution of pH 5·8–6·0 was prepared from 0·2 M acetic acid and 0·2 M sodium acetate.

Apparatus

A Hilger U.V. Speck spectrophotometer with 1 cm. quartz absorption cells and Elico (L1–10) pH meter with a beckman glass electrode were used for optical density and pH measurements respectively.

Identification and Dilution Limits

The limits of identification and dilution were determined as follows:

A drop of the germanium solution was placed on a spot plate and a drop of sodium acetate solution (0·1%) added followed by a drop of 0·05% reagent solution. Orange to yellow precipitate was obtained depending on the amount of metal present. A blank was run simultaneously which showed only an yellow colour (colour of the reagent).

Limit of identification	0·625 γ (0·05 ml.)
Limit of dilution	1 : 80,000

Absorption Spectrum of the Complex

5 ml. of the germanium solution ($2 \cdot 0 \times 10^{-4}$ M) were mixed with 20 ml. of the reagent solution of the same concentration. The optical density values were recorded at different wavelengths (380 mμ–490 mμ), using reagent solution as blank (20 ml. of $2 \cdot 0 \times 10^{-4}$ M solution diluted to 25 ml.), and reported in Table 1; Fig. 1. The maximum absorption was at 400 mμ.

TABLE I

Wavelength (mμ)	Optical density
380	0·300
390	0·630
400	0·682
410	0·585
420	0·465
430	0·345
440	0·270
450	0·205
460	0·158
470	0·120
480	0·090
490	0·070

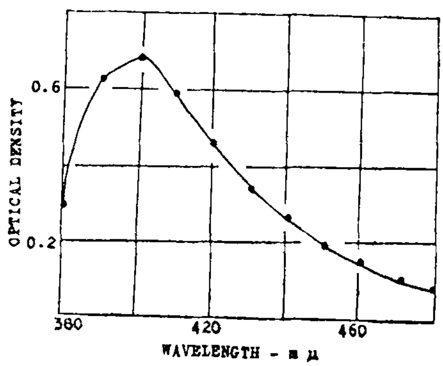


FIG. 1

Influence of pH on the Complex Formation

1 ml. of germanium solutio ($5 \cdot 0 \times 10^{-4}$ M) was mixed with 5 ml. of reagent solution ($5 \cdot 0 \times 10^{-4}$ M) and made up to 25 ml. with alcohol after

adjusting the pH of the solution to a desired value. Reagent of the same concentration was used as the blank. The values of optical density at different pH values up to 6·0 are reported in Table II; Fig. 2. The reagent itself gave an orange-yellow colour above pH 6·0. The pH of the solutions were kept between 5·8–6·0 using the buffer in all other investigations.

TABLE II

pH	Optical density (400 mμ)
3·0	0·375
4·0	0·385
5·0	0·390
5·5	0·690
6·0	0·690

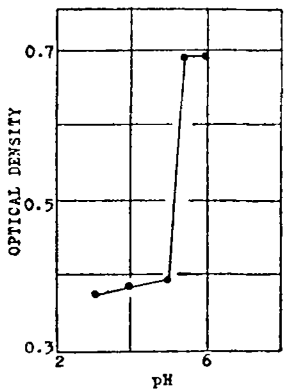


FIG. 2

Verification of Beer's Law

Solutions containing 1·0–10·0 p.p.m. of germanium were taken and the reagent was added in excess (1·5 ml. of 0·001 M). The solution was made up to 25 ml. using the buffer after adding 12·0 ml. of alcohol to maintain 50% alcoholic concentration. Optical density measurements were made at 400 mμ against the reagent blank (1·5 ml. of 0·001 M made up to 25 ml. with alcohol). The results are reported in Table III. The optical density values are plotted against p.p.m. of germanium. The relationship between concentration of germanium and optical density is linear up to 6·0 p.p.m. (Fig. 3). Beer's Law is, therefore, obeyed only in the range of 1·0–6·0 p.p.m. of germanium.

TABLE III

Germanium (p.p.m.)	Optical density (400 mμ)
1·0	0·070
2·0	0·140
3·0	0·165
4·0	0·200
5·0	0·218
6·0	0·250
7·0	0·242
8·0	0·262
9·0	0·270

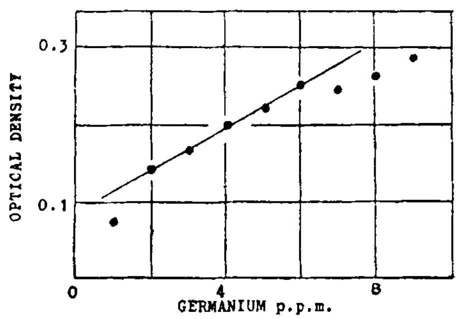


FIG. 3

Molar composition of the complex

Method of continuous variations (*Job*[3]).—The molar composition of the complex was determined by Job's method of continuous variations using $1{\cdot}0 \times 10^{-3}$ M solutions of germanium and reagent in one set of experiments and $5{\cdot}0 \times 10^{-4}$ M solutions in the second set. In all cases the solutions were made up to 25 ml. after the addition of 12·0 ml. of alcohol, with the buffer. The optical densities were measured at 400 mμ and the data reported in Table IV; Fig. 4. Reagent correction was applied for all the optical density values.

TABLE IV

Reagent (ml.)	Metal (ml.)	Optical density (corrected values) (400 mμ)	
		$1{\cdot}0 \times 10^{-3}$ M.	$5{\cdot}0 \times 10^{-4}$ M.
1·0	9·0	0·390	0·252
2·0	8·0	0·660	0·329
3·0	7·0	1·100	0·438
4·0	6·0	1·280	0·658
5·0	5·0	1·500	0·735
6·0	4·0	1·580	0·847
7·0	3·0	1·700	0·864
7·5	2·5	1·750	0·883
8·0	2·0	1·600	0·812
9·0	1·0	1·150	0·343

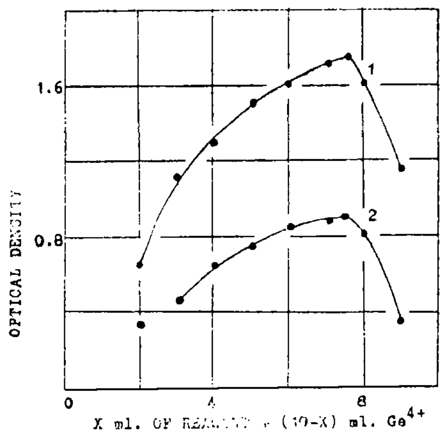


FIG. 4. (1) $1{\cdot}0 \times 10^{-3}$ M; (2) $5{\cdot}0 \times 10^{-4}$ M.

TABLE V

Reagent or Ge (ml.)	Optical density (400 mμ)	
	Excess reagent	Excess Ge
0·2	0·190	0·062
0·4	0·360	0·122
0·6	0·540	0·185
0·8	0·720	0·230
1·0	0·840	0·315

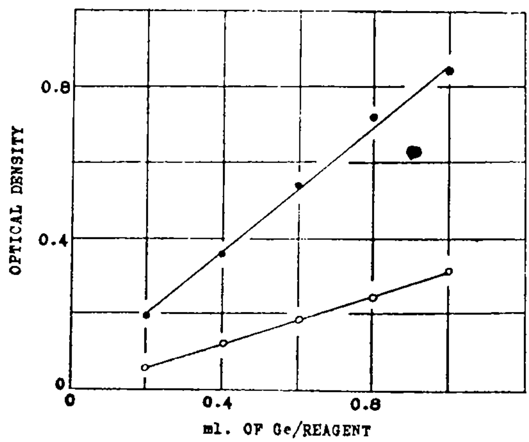


FIG. 5. O——O With Excess Ge; ●——● With Excess Reagent.

The optical density values in both the sets of experiments are maximum when the molar ratio of the reagent to metal is 3: 1.

Slope ratio method (*Harvey and Manning*[4]):—Two series of solutions were prepared using 1·0 × 10^{-3} M solutions of the reagent and metal ion.

In the first series, 5·0 ml. of the reagent (large excess) was treated with 0·2, 0·4, 0·6, 0·8 and 1·0 ml. of the metal ion solution, 8·0 ml. of alcohol and the solution made up to 25 ml. with buffer. The alcohol content was adjusted to 50% by volume in all cases. Reagent solution (5·0 ml. of

10^{-3} M in 25 ml. of alcohol) was used as blank. Optical densities were recorded at 400 mμ against the reagent blank.

In the second series, 5·0 ml. of metal ion solution (large excess) was treated with 0·2, 0·4, 0·6, 0·8 and 1·0 ml. of the reagent solution and 12·0 ml. of alcohol were added and the solution made up to 25 ml. with buffer. The alcohol content was adjusted to 50% by volume in all cases. In this case water alone was used as blank. Optical densities were recorded at 400 mμ and the data obtained in both the series are reported in Table V.

In both the cases the optical density values were plotted against the added metal ion or reagent as the case may be (Fig. 5). The two plots were linear. The slopes of the two curves were calculated. The ratio of the slopes gave a value of 3·061. The combining ratio of the reagent to metal is, therefore, 3 : 1.

Instability Constant or the Complex (Edmonds and Birnbaum[5]*)*

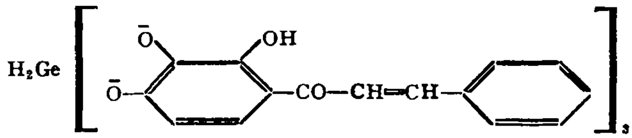
Solutions containing for the same amount of germanium (2 ml. of $5{\cdot}0 \times 10^{-4}$ M) different amounts of reagent (excess) were prepared. The pH was adjusted to 5·8–6·0 with the buffer, 1·0 ml. of 0·1 M solution of potassium perchlorate was added to suppress the dissociation of the complex, and the solutions were made up to 25 ml. Optical density measurements were made at 400 mμ. The data are reported in Table VI. Instability constants were calculated in pairs of cases and the average value is $1{\cdot}670 \times 10^{-11}$ at 28° C.

TABLE VI

Sl. No.	Reagent (ml.) 5×10^{-4} M.	Optical density (400 mμ)
1	5·0	0·495
2	7·5	0·800
3	10·0	0·900
4	15·0	1·200
5	20·0	1·450

STRUCTURE OF THE COMPLEX

The author found that gallacetophenone, 2′-hydroxy chalcone and 2′, 4′-dihydroxy chalcone did not yield any precipitate with germanium, whereas 2′, 3′, 4′-trihydroxy chalcone gave an yellow precipitate from weakly acid solutions. Bevillard,[1] however, reported that chloro-gallacetophenone yielded a maroon coloured precipitate. By analogy with the conclusions of Takuji Kanno[7,8] that complex formation with germanium in neutral or weakly acid solution involved two hydroxyls in *ortho*-positions and the carbonyl group played no part, it is concluded that the structure of the germanium-chalcone complex is probably as follows:



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