

On the Oxyanion Chelates of *o*-Diphenols

I. Chelate Formation by Protocatechualdehyde with Oxyacids

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The ability of protocatechualdehyde to form anionic chelates with arsenious, boric, and germanic acids in aqueous 0.1 M potassium chloride solutions has been studied potentiometrically. It appears that boric acid and arsenious acid form one-to-one monobasic chelate acids. Germanic acid, however, forms a one-to-three (germanic acid to ligand) dibasic chelate. The formation constants of all the above-mentioned chelates were determined. The first protolytic constant of protocatechualdehyde was likewise determined. The following values were obtained for the constants in 0.1 M potassium chloride solutions at 25°C:

$$\begin{aligned} K_{\text{HA}} &= [\text{H}^+][\text{HL}^-]/[\text{H}_2\text{L}] = 6.042 \times 10^{-8} \\ K_{\text{I}} &= [\text{H}^+][\text{AsL}^-]/[\text{HAsO}_3][\text{H}_2\text{L}] = 6.668 \times 10^{-7} \\ K_{\text{I}} &= [\text{H}^+][\text{BL}^-]/[\text{H}_3\text{BO}_3][\text{H}_2\text{L}] = 1.118 \times 10^{-4} \\ K_{\text{III}} &= [\text{H}^+]^3[\text{GeL}_3^{2-}]/[\text{H}_2\text{GeO}_3][\text{H}_2\text{L}]^3 = 604.0 \end{aligned}$$

It is known from earlier investigations¹⁻³ that *o*-diphenols have a marked tendency to form anionic chelates with some inorganic oxyacids. The best known of these acids that form anionic chelates are arsenious, boric, and germanic acids. The aim of this investigation was to clarify the anionic chelate formation reactions of the mentioned acids with protocatechualdehyde and to compare the results with those for other similar anionic chelate formation reactions.

EXPERIMENTAL

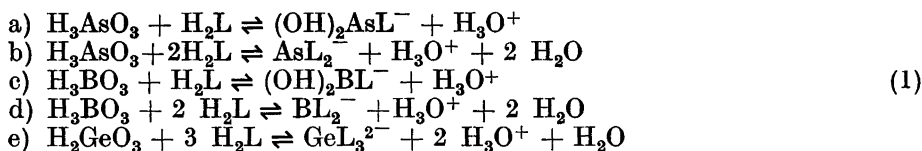
The measurements were carried out at 25°C on aqueous solutions containing varying concentrations of ligand and oxyacid in which the ionic strength was stabilized by making the solution 0.1 M in potassium chloride.

All reagents used, with the exception of protocatechualdehyde, were of analytical grade and were used without further purification. The protocatechualdehyde, m.p. 151–152°C, samples of which were obtained from both Fluka AG and Nipa laboratories Ltd., was purified with active charcoal, crystallized from water, and washed with toluene containing a little ethanol. The product was then recrystallized four times from toluene, and finally dried at 100°C under reduced pressure using paraffin and phosphorus pentoxide

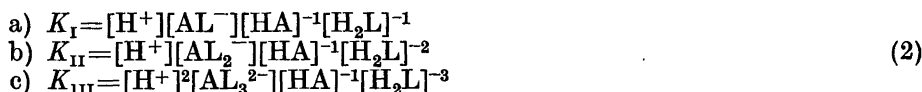
as drying agents. The melting point of the crystalline substance was 153.5–154°C. It was found by thin layer chromatography that the product contained only negligible quantities of impurities and apparently no protocatechuic acid, which could have interfered with the pH measurements. All solutions were prepared in distilled water free from dissolved oxygen. Also the vessels used for storage of the solutions were flushed with nitrogen to remove the air. Carbon dioxide and oxygen were removed by leading purified nitrogen through the solutions before and solutions, 50 ml in volume containing protocatechualdehyde and the studied oxyacid were titrated with 0.1 N sodium hydroxide. The temperature was maintained at 25°C with a water thermostat. The pH measurements during the titrations were carried out with a Radiometer Type PHM 4c pH meter and a Beckman Type E2 No. 41263 glass electrode. A Beckman Type K100 calomel electrode was used as reference electrode. As reference solution, a 0.05 M potassium hydrogen phthalate solution (pH=4.012) was used. When calculating the hydrogen ion concentrations from the measured pH values, the value of the apparent activity coefficient $\gamma_{\text{H}^+} = 0.081$ (0.1 M potassium chloride)⁴ was used. Previously determined values, 7.35×10^{-10} , 8.00×10^{-10} , and 2.63×10^{-10} , of the first protolytic constants of arsenious,⁵ boric,⁶ and germanic⁷ acids, respectively, in 0.1 M potassium chloride solutions at 25°C were used in computing the equilibrium constants.

THEORY

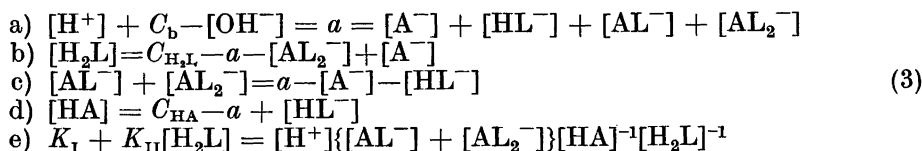
According to earlier studies, it was expected that arsenious,^{5,8} boric,⁹ and germanic¹⁰ acids would react with protocatechualdehyde as follows:



The equilibrium constants corresponding to these reactions can be expressed as



where HA denotes the studied oxyacid, and AL^- , AL_2^- , and AL_3^{2-} the formed 1:1, 1:2 and 1:3 chelates, respectively. In order to evaluate the mentioned chelation constants, titrations were carried out on solutions containing varying concentrations of protocatechualdehyde and the oxyacids in question. The equilibrium constants K_{I} and K_{II} were evaluated with the aid of the following equations:⁹



In these equations, in addition to the foregoing notations, C_{b} , $C_{\text{H}_2\text{L}}$, and C_{HA} denote the stoichiometric concentrations of the added alkali, the ligand, and the oxyacid respectively. When calculating the term $[\text{H}_2\text{L}]$ it was assumed that the term $[\text{AL}_2^-]$ is negligible compared to the other terms in eqn. (3b). The following equations were then obtained:

Table 1. A typical series of data for the determination of the first ionization constant of protocatechualdehyde in 0.1 M KCl solutions at 25°C.

$C_{\text{H}_2\text{L}} \times 10^3$	$a \times 10^3$	pH	$\text{p}K_1$
9.804	1.961	6.600	(7.553)
9.615	3.846	7.039	7.215
9.524	4.762	7.217	7.217
9.434	5.660	7.394	7.218
9.260	7.406	7.827	7.225
9.174	8.255	8.189	(7.236)
			Average 7.190

$$\begin{aligned}
 [\text{HA}] &= C_{\text{HA}} - a + K_{\text{H}_2\text{L}} [\text{H}_2\text{L}][\text{H}^+]^{-1} \\
 [\text{H}_2\text{L}] &= C_{\text{H}_2\text{L}} - a + \frac{K_{\text{HA}}}{[\text{H}^+]} (C_{\text{HA}} - a) \left(1 - \frac{K_{\text{HA}} K_{\text{H}_2\text{L}}}{[\text{H}^+]^2} \right) \quad (4)
 \end{aligned}$$

where K_{HA} and $K_{\text{H}_2\text{L}}$ are the first protolytic constants of the oxyacid and the ligand, respectively.

The equilibrium constant of the chelation of germanic acid conforming to eqn. (2c), was evaluated by substituting the titration data in the earlier derived equation¹⁰

$$K_{\text{III}} = 0.5 a [\text{H}^+]^2 (C_{\text{H}_4\text{GeO}_4} - 0.5 a)^{-1} (C_{\text{H}_2\text{L}} - 1.5 a)^{-3} \quad (5)$$

RESULTS

1. *Protolysis of protocatechualdehyde.* Values of the first protolytic constant of protocatechualdehyde calculated from titration data are presented in Table 1. The obtained mean value $K_1 = 6.042 \times 10^{-8}$ (in 0.1 M KCl) was used in the following calculations of the chelation constants.

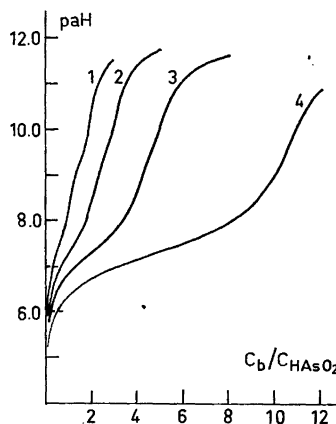


Fig. 1. Titration data for solutions containing different molar ratios of arsenious acid and protocatechualdehyde. 1) 1:1; 2) 1:2; 3) 1:4; and 4) 1:10.

Table 2. Two typical series of data for the determination of the equilibrium constants of the reaction between arsenious acid and protocatechualdehyde in 0.1 M KCl solutions at 25°C. (cf. eqns. (2) and (3)).

C_{HAsO_2} $\times 10^3$	$C_{\text{H}_2\text{L}}$ $\times 10^3$	$a \times 10^3$	pH	$[\text{HAsO}_2]$ $\times 10^3$	$[\text{H}_2\text{L}]$ $\times 10^3$	$(K_I + K_{II}[\text{H}_2\text{L}])$ $\times 10^7$
9.901	9.901	0.9907	6.201	9.766	8.920	8.896
9.804	9.804	1.961	6.551	9.532	7.863	9.268
9.615	9.615	3.846	6.979	9.125	5.832	8.405
9.434	9.434	5.660	7.325	8.768	3.911	7.314
9.260	9.260	7.406	7.694	8.289	2.154	7.602
9.174	9.174	8.256	7.942	8.742	1.480	(11.48)
				Average	5.027	8.827
4.950	19.80	0.9914	5.902	4.866	18.81	11.16
4.902	19.60	1.962	6.225	4.730	17.65	11.85
4.854	19.42	2.913	6.433	4.644	16.51	9.675
4.808	19.23	3.846	6.584	4.533	15.40	9.779
				Average	17.09	10.61

2. *Arsenious acid-protocatechualdehyde chelate.* Fig. 1 shows curves plotting data from titrations of different arsenious acid-protocatechualdehyde solutions with alkali. Two typical series of data for calculating the chelation constants defined by eqns. (2) are presented in Table 2. The results of all titrations obtained as shown in Table 2 are collected in Table 3. As the expression $K_I + K_{II}[\text{H}_2\text{L}]$ (cf. eqn. (3e)) appears to remain constant regardless of the ligand concentration, it is obvious that mainly a one-to-one chelate, the formation constant of which is $K_I = 6.668 \times 10^{-7}$ (in 0.1 M KCl), is formed.

3. *Boric acid-protocatechualdehyde chelate.* Curves plotting data from titrations of different boric acid-protocatechualdehyde solutions with alkali are shown in Fig. 2. Two series of data for calculating the constants K_I and K_{II} (cf. eqn. (2)) are presented in Table 4. The final results of the titrations are collected in Table 5. As the expression $K_I + K_{II}[\text{H}_2\text{L}]$ (cf. eqn. (3e)) appears

Table 3. Experimental data for the determination of the equilibrium constant K_I of the reaction between arsenious acid and protocatechualdehyde in 0.1 M KCl solutions at 25°C.

$[\text{HAsO}_2] \times 10^3$	$[\text{H}_2\text{L}] \times 10^3$	$p(K_I + K_{II}[\text{H}_2\text{L}])$
36.58	4.894	6.424
9.037	5.027	6.059
18.93	5.984	6.522
9.027	14.37	6.121
4.693	17.09	5.978
4.688	46.36	5.950
		Average 6.176

Table 4. Two typical series of data for the determination of the equilibrium constants of the reaction between boric acid and protocatechualdehyde in 0.1 M KCl solutions at 25°C. (cf. eqns. (2) and (3)).

$C_{\text{H}_3\text{BO}_3} \times 10^3$	$C_{\text{H}_2\text{L}} \times 10^3$	$a \times 10^3$	pH	$[\text{H}_3\text{BO}_3] \times 10^3$	$[\text{H}_2\text{L}] \times 10^3$	$(K_I + K_{\text{II}}[\text{H}_2\text{L}]) \times 10^4$
9.804	9.804	1.965	5.423	7.966	7.841	1.100
9.615	9.615	3.847	5.952	6.079	5.772	1.129
9.524	9.524	4.763	6.202	5.221	4.767	1.085
9.434	9.434	5.660	6.432	4.392	3.784	1.120
9.260	9.260	7.407	6.997	2.977	1.874	1.091
				Average	4.808	1.105
4.902	19.61	1.961	5.433	3.230	17.65	1.082
4.808	19.23	3.846	5.971	1.831	15.39	1.129
4.762	19.05	4.762	6.194	1.349	14.27	1.132
4.717	18.87	5.660	6.390	1.016	13.21	1.123
4.630	18.52	7.407	6.697	0.5650	11.11	1.300
				Average	14.33	1.153

to be independent of ligand concentration, boric acid forms with protocatechualdehyde a one-to-one chelate, the formation constant of which is $K_I = 1.118 \times 10^{-4}$ (in 0.1 M KCl).

4. *Germanic acid-protocatechualdehyde chelate.* Curves plotting data from titrations of different solutions of germanic acid-protocatechualdehyde with alkali are shown in Fig. 3. It can be seen directly from these curves that the reaction occurs in conformity with eqn. (1e). This is in agreement with the two series of titration data in Table 6, from which nearly identical values are obtained for the constant K_{III} in different conditions. The values of K_{III} thus calculated from different titrations are collected in Table 7. Germanic acid hence forms a chelate mainly in accordance with eqn. (1e); the formation

Table 5. Experimental data for the determination of the equilibrium constant K_I of the reaction between boric acid and protocatechualdehyde in 0.1 M KCl solutions at 25°C.

$[\text{H}_3\text{BO}_3] \times 10^3$	$[\text{H}_2\text{L}] \times 10^3$	$p(K_I + K_{\text{II}}[\text{H}_2\text{L}])$
1.612	2.412	3.921
5.327	4.808	3.956
19.23	4.808	3.970
1.612	4.818	3.952
42.97	4.803	3.970
1.655	14.33	3.937
1.577	23.86	3.976
5.327	24.12	3.956
0.9666	42.91	3.919
		Average 3.951

Table 6. Two typical series of data for the determination of the equilibrium constants of the reaction between germanic acid and protocatechualdehyde in 0.1 M KCl solutions at 45°C (cf. eqn. (4) and (5)).

$C_{H_2GeO_3} \times 10^3$	$C_{H_2L} \times 10^3$	$[H^+] \times 10^3$	$a \times 10^3$	$\log K_{III}$
5.000	10.00	4.819	4.819	3.006
4.950	9.901	4.286	4.781	2.927
4.902	9.804	3.828	4.808	2.908
4.854	9.709	3.436	4.892	2.954
4.808	9.615	2.965	4.888	2.883
4.762	9.524	2.535	4.916	2.839
4.717	9.434	2.143	4.974	2.824
4.673	9.346	1.726	4.997	2.733
4.630	9.260	1.387	5.091	2.712
4.587	9.174	1.028	5.156	2.649
4.545	9.091	0.6982	5.243	2.557
				Average 2.818
10.00	3.000	13.65	13.65	(2.666)
9.901	2.970	13.12	14.11	2.838
9.804	2.941	12.02	13.98	2.776
9.709	2.913	11.40	14.31	2.909
9.615	2.885	10.47	14.32	2.904
9.524	2.857	9.616	14.38	2.919
9.434	2.830	8.590	14.25	2.837
9.346	2.804	7.798	14.34	2.851
9.260	2.778	7.047	14.45	2.890
9.174	2.752	6.180	14.44	2.846
9.091	2.727	5.470	14.56	2.876
9.010	2.703	4.656	14.57	2.821
8.929	2.678	3.954	14.67	2.821
8.850	2.655	3.243	14.75	2.785
8.772	2.632	2.570	14.85	2.742
8.696	2.609	1.950	14.99	2.706
8.621	2.586	1.346	15.14	(2.621)
				Average 2.835

Table 7. Values of the equilibrium constant K_{III} of the reaction between germanic acid and protocatechualdehyde in 0.1 M KCl solution at 25°C.

$C_{H_2GeO_3} \times 10^3$	$C_{H_2GeO_3}:C_{H_2L}$	$\log K_{III}$
4.766	1:2	2.818
4.783	1:3	2.792
9.198	1:3	2.771
9.274	1:3	2.835
4.833	1:4	2.697
4.760	1:6	(1.696)
4.774	1:10	(0.8..)
		Average 2.782

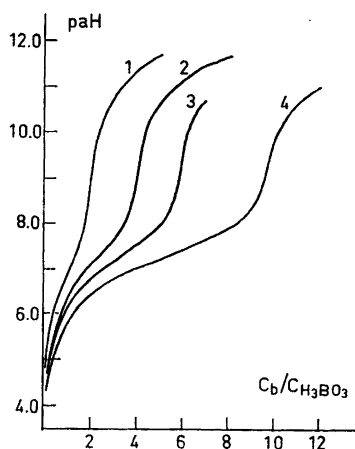


Fig. 2. Titration data for solutions containing different molar ratios of boric acid and protocatchualdehyde. 1) 1:2; 2) 1:4; 3) 1:6; and 4) 1:10.

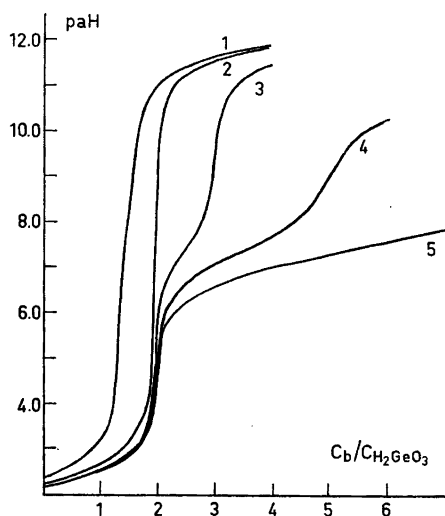


Fig. 3. Titration data for solutions containing different molar ratios of germanic acid and protocatchualdehyde. 1) 1:2; 2) 1:3; 3) 1:4; 4) 1:6; and 5) 1:10.

constant of the chelate has the value $K_{III}=604.0$ (in 0.1 M KCl). It should be noted, however, that values deviating from this are obtained from data for solutions containing a great excess of the ligand and that the values of the constant K_{III} calculated from data at different points on the titration

Table 8. Values of chelation constants of chelates formed by arsenite borate and germanate ions with some *o*-diphenols (25°C, cf. eqns. (2) and (6)).

Ligand	Arsenite		Borate		Germanate log K_{III} (in 0.1 M KCl)	References
	log k_1°	log k_2°	log k_1°	log k_2°		
Catechol (I)	2.242	2.708	3.972	4.263	-0.773	5,9,10
Tiron (II)	—	1.108	4.90	—	2.740	8,3,10
Protocatechualdehyde (III)	2.958	—	5.145	—	2.782	This paper

I

II

III

curve do not remain constant. This indicates that also other chelates than the one-to-three chelate are formed when the molar ratio of germanic acid and protocatechualdehyde is low. The same observation has been made earlier¹⁰ when other diphenol chelates of germanic acid have been investigated.

CONCLUSIONS

The foregoing results show that arsenious acid and boric acid form mainly monobasic one-to-one chelate acids with protocatechualdehyde, whereas germanic acid appears to have a tendency to form a divalent one-to-three (acid to ligand) chelate acid with the ligand. The values of the chelation constants obtained in this investigation are presented together with some earlier determined chelation constants of *o*-diphenol chelates in Table 8. It is noted on comparing these constants that a carbonyl group clearly promotes chelate formation by *o*-diphenols with arsenious, boric, and germanic acids. When computing the data in Table 8, the relation

$$K_1/K_{HA} = [AL^-] \cdot [A^-]^{-1} \cdot [H_2L]^{-1} = k_1^\circ \quad (6)$$

where K_{HA} is the protolytic constant of the oxyacid, was used to calculate the chelation constants k_1° of the arsenious and boric acid chelates. Thus the chelation constant k_1° refers to the reaction



where the anion of the oxyacid reacts with the ligand. As no change in charge occurs in the reaction, the equilibrium constants can be considered thermodynamic constants.

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