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OXALATO-COMPLEXES OF TANTALUM

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Many stable complexes of tantalum are known, and the compositions of some have been established. As with other elements with high valencies, however, there are almost no data on the stability of the compounds, that is, on the quantitative characteristics of the complex-formation equilibria. This is due chiefly to the difficulty of establishing the composition and concentration of the ionic forms in the solution. We previously studied the solubility and acid–base dissociation of niobium and tantalum hydroxides[1]. Their solubility in acids is due to the binding of the hydroxide ions of the $M(OH)_5$; the change in solubility in the presence of complex-forming reagents allows the stability of the complexes to be calculated. The first material to be studied was the oxalato-complex of tantalum.

The ions of elements with high valencies are extensively hydrolysed in aqueous solutions, so that when these ions react with various ligands, we should expect the formation of a series of complexes consisting of the products of the displacement of OH^- ions by ions of the complex-forming reagent, or the products of the attachment of the ligand to hydrolysed metal ions. In such cases it becomes necessary to study ternary complexes in systems of the type M–OH–A. These ternary complexes may dissociate with the removal of OH or A, or both, and each of these processes should be characterised by a definite dissociation constant (the instability constant of the complex). To denote the consecutive k and cumulative K instability constants of ternary complexes of the type $M(OH)mAn$, we propose the following symbols:

$$^{m}k_{nA}, \quad ^{nA}k_{mB}, \quad ^{m}K_{nA}, \quad ^{nA}K_{mB}.$$

The letters A and B denote A and OH groups respectively. The letters n and m used as right-hand subscripts denote the number of A or OH groups respectively in the original complex; the left-hand subscript letters n and m denote the number of A or OH groups respectively remaining after dissociation in the complex. Examples of some constants for the complex $M(OH)_3A_2$ are:

$$^{13}k_{1A} = \frac{[M(OH)_3A][A]}{[M(OH)_3(A)_2]}, \quad ^{13}K_{3A} = \frac{[M(OH)_3][A]^2}{[M(OH)_3(A)_2]},$$

$$^{1A}k_{1B} = \frac{[M(OH)_2(A)_2][OH]}{[M(OH)_3(A)_2]}, \quad ^{1A}K_{3B} = \frac{[M(A)_2][OH]^2}{[M(OH)_3(A)_2]}.$$

The appropriate constant for the dissociation of the complex according to any scheme can be represented similarly.

A large number of methods for separating tantalum from accompanying elements[2,3], and for its analytical determination[4], are based on the formation of oxalato-complexes. In an excess of oxalic acid with concentration 0.3 M, these complexes are anionic and contain 2 g-ions of oxalate per g-atom of tantalum[5]. It has been reported that the oxalato-complex of tantalum is less stable than the niobium complex[6], but there are no quantitative data on the equilibria.

In our experiments we used data obtained in our earlier work[1], where it was shown that change in temperature (17–25°) and duration of contact (10–40 d) is almost without influence on the solubility of tantalum hydroxide. The tantalum hydroxide was prepared by adding nitric acid to a known quantity of potassium tantalate solution to pH 4–5, and was washed several times by decantation and centrifuging. A suspension of it was prepared by shaking, and transferred to an oxalic acid solution of known pH. Generally the acidity was checked with a glass electrode. The total volume of solutions and precipitates amounted to 100 ml, and the temperature used was 18–20°. To attain equilibrium, the mixtures were generally kept for 2 months. The total concentration of tantalum hydroxide added corresponded to 1.5×10^{-3} M. After 2 months, the precipitates were separated by centrifuging. The equilibrium concentration of tantalum in the solution and its concentration in the precipitate were determined photometrically as the pyrocatechol–oxalato-complex[7,8]. The concentration of oxalate in the solution and precipitate was determined by titration with 0.01 N permanganate.

Influence of pH on the Formation of Soluble Oxalato--Complexes of Tantalum

We first studied the pH range in which soluble oxalato--complexes of tantalum are formed in an excess of oxalate with a concentration of 0.1 M. The results are represented by curve 1 in Fig. 1, and curve 2 gives for comparison the solubility of tantalum hydroxide in the absence of oxalic acid (data obtained earlier). Curve 3 gives the solubility, in the absence of an excess of oxalic acid, of the solid phase formed under the above conditions; these data are discussed in detail below.

The range of existence of soluble oxalato-complexes of tantalum is fairly narrow; the optimal conditions correspond to the pH range 0–3.5 (Fig. 1). This result is evidently related to the acidic properties of oxalic acid, for which $pK_1 = 1.4$ and $pK_2 = 4.4$. It can readily be shown that the interconversion of the different forms of oxalic acid in solution corresponds to the following value of $pH_{1/2}$
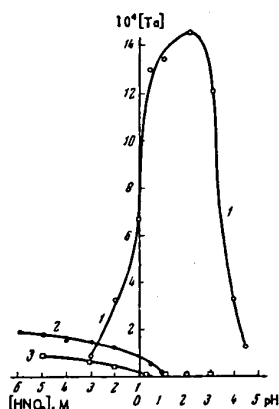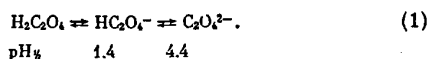
Fig. 1. Solubility of tantalum hydroxide and oxalato-complexes of tantalum. $[Ta]_{total}$ = $= 1.5 \times 10^{-3}$ g-atom litre^{-1}:
1) $Ta(OH)_5$ in 0.1 M $H_2C_2O_4$; 2) $Ta(OH)_5$ without oxalate; 3) $Ta(OH)_3(C_2O_4)$.

(the pH at which the concentrations of successive forms are equal):

$$H_2C_2O_4 \rightleftharpoons HC_2O_4^- \rightleftharpoons C_2O_4^{2-}. \tag{1}$$

$$pH_{1/2} \qquad 1.4 \qquad 4.4$$

In strongly acidic medium at pH < 1.4, the concentration of free $C_2O_4^{2-}$ ions is proportional to the square of the change in the hydrogen ion concentration; this evidently leads to decomposition of the soluble oxalato-complex in strongly acidic medium and explains the descending left-hand branch of curve 1. At pH ≥ pK_2, oxalic acid is converted almost completely into $C_2O_4^{2-}$ ions and their concentration does not increase with further increase in pH (at constant total $H_2C_2O_4$ concentration). At the same time, increase in pH continues to increase the concentration of OH^- ions, which displace $C_2O_4^{2-}$ from the coordination sphere. The slight displacement of the corresponding pH values towards more acidic values relative to $pH_{1/2}$ is quite usual for equilibria of this type, and is due to complex-formation by Ta^V with $C_2O_4^{2-}$.

Composition of the Solid Phase in Equilibrium with Oxalate

Subsequent experiments confirmed in general the nature of the equilibria disclosed. More detailed study, however, reveals significant characteristic features of this system. In the reaction between a solid phase and a ligand which binds the metal in a complex, the composition of the solid phase usually remains constant. By analogy with the usual cases, it might have been expected that the complex in solution in equilibrium with the solid phase $Ta(OH)_5$ would be the simplest complex, for example, $Ta(OH)_4(C_2O_4)^-$. The data given below, however, show that the first stage in complex formation involves not the formation of a soluble complex but the transfer of ligand to the solid phase; the monooxalato-complex of tantalum is a sparingly soluble compound.

Table 1 gives the results of a study of the equilibria at various oxalic acid concentrations over a wide range of

TABLE 1. Solubility of tantalum hydroxide in oxalic acid at various pH.

$[H_2C_2O_4]_{total} \times 10^3$, M	2 N HNO3			1 N HNO3			0.5 N HNO3		
1	2	3	4	5	6	7	8	9	10
	10^4 [Ta] in solution	10^3 [H2C2O4] in solution	Ta:C2O4^{2-} in precipitate	10^4 [Ta] in solution	10^3 [H2C2O4] in solution	Ta:C2O4^{2-} in precipitate	10^4 [Ta] in solution	10^3 [H2C2O4] in solution	Ta:C2O4^{2-} in precipitate
0.5	0.39	0.35	1.00	0.22	0.34	0.94	0.12	0.35	1.00
0.8	0.42	0.65	1.00	0.32	0.64	0.94	0.20	0.64	0.94
1.0	0.49	0.84	0.94	0.40	0.85	1.00	1.13	0.85	1.00
1.6	0.59	1.46	1.07	0.65	1.45	1.00	1.46	1.87	1.15
4.0	1.19	3.88	1.25	1.97	3.86	1.07	4.35	3.86	1.07
6.0	1.65	5.86	1.07	3.05	5.85	1.00	6.86	5.87	1.15
8.0	2.40	7.88	1.15	4.50	7.87	1.15	9.20	7.86	1.07
10.0	3.22	9.90	0.94	6.16	9.90	0.94	11.00	9.90	0.94

| $[H_2C_2O_4]_{total} \times 10^3$, M	pH 1.0			pH 2.0			pH 4.0		
1	11	12	13	14	15	16	17	18	19
	10^4 [Ta] in solution	10^3 [H2C2O4] in solution	Ta:C2O4^{2-} in precipitate	10^4 [Ta] in solution	10^3 [H2C2O4] in solution	Ta:C2O4^{2-} in precipitate	10^4 [Ta] in solution	10^3 [H2C2O4] in solution	Ta:C2O4^{2-} in precipitate
0.5	0.21	0.36	1.07	0.23	0.34	0.94	0.10	0.37	1.15
0.8	0.38	0.63	0.88	0.38	0.67	1.15	0.18	0.66	1.07
1.0	0.69	0.84	0.94	0.63	0.87	1.15	0.27	0.86	1.07
1.6	1.55	1.45	1.00	1.18	1.46	1.07	0.41	1.45	1.00
4.0	4.47	3.86	1.07	5.52	3.87	1.15	1.28	3.86	1.07
6.0	7.03	5.85	1.00	9.47	5.85	1.00	1.94	5.84	0.94
8.0	9.45	7.88	1.25	13.00	7.88	1.25	2.48	7.87	1.15
10.0	11.30	9.87	1.15	14.60	9.87	1.15	3.24	9.89	0.94

Note. All concentrations are given in mole litre^{-1}.

acidity. The total tantalum concentration corresponded to 1.5×10^{-3} g-atom litre^{-1}. Comparison of column 1 with columns 3, 6, 9, 12, 15, and 18 shows that the concentration of oxalic acid in the solution is always less than the original concentration. Some of the added oxalate is always transferred to the precipitate. In addition to careful analysis of the solutions, we also analysed all the precipitates, after centrifuging and washing them with water. All these data (Table 1) show that when oxalic acid is added, tantalum hydroxide is converted into a compound with an even lower solubility; in this solid phase the ratio Ta:$C_2O_4^{2-}$ = $= 1:1$. The formation of this compound explains a number of properties of tantalum hydroxide. In particular, it is known that in the precipitation of tantalum hydroxide from oxalate or fluoride solutions, it is extremely difficult to wash the resulting hydroxides free from oxalate or fluoride. The above data show that the difficulty of removing certain anions from a tantalum hydroxide precipitate is due not to simple adsorption but to the formation of a chemical compound which is less soluble than pure tantalum hydroxide.

To confirm this view of the reaction, we determined the quantity of OH^- ions displaced by oxalate ions from tantalum hydroxide. A pH of 2 was established at the start of all the experiments. The oxalate was taken in twofold excess relative to the tantalum hydroxide. Analysis of the solutions over the precipitates showed that appreciable quantities of soluble tantalum complex are not formed. The pH of these mixtures increases considerably on standing. The addition of 0.5 N nitric acid restored the initial pH of 2. The increase in pH stopped after 10–12 days.

From the quantity of nitric acid used, it was found that 1 g-equiv. of OH⁻ ions is liberated in the mixtures per g-atom of tantalum.

From the values of pK for oxalic acid, it can be seen [Eqn. (1)] that at pH 2 oxalic acid exists chiefly as the hydrogen oxalate ion. The reaction thus takes place according to the equation

$$Ta(OH)_5 + HC_2O_4^- = Ta(OH)_3(C_2O_4) + OH^- + H_2O. \qquad (2)$$
solid phase   solid phase
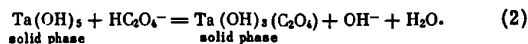
Solubility and Dissociation of Ta(OH)₃(C₂O₄)

The direct determination of the solubility of the compound $Ta(OH)_3(C_2O_4)$ is difficult, because of the formation of colloidal suspensions and, possibly, polyionic complexes in the absence of an excess of oxalate. We therefore tried to calculate the solubility. The data in Table 1 were used to construct a graph (Fig. 2) giving the dependence of the equilibrium concentration of tantalum on the ratio $H_2C_2O_{4\,total} : Ta_{total}$.

Extrapolation of the values obtained to zero concentration of free ligand shows that the solubility of the compound $Ta(OH)_3(C_2O_4)$ is 4×10^{-6} M. The solubility of $Ta(OH)_5$ is 6×10^{-6} M.[1] The slightly lower solubility of $Ta(OH)_3(C_2O_4)$ corresponds to the formation of this compound in the presence of even small quantities of oxalic acid.

These solubility data reflect the properties of the molecular form only of the compound $Ta(OH)_3(C_2O_4)$. To find how it dissociates, we measured its solubility in acids in the absence of an excess of oxalic acid. The results (curve 3 in Fig. 1) confirm that the solubility of $Ta(OH)_3(C_2O_4)$ is less than that of tantalum hydroxide (compare curves 3 and 2 in Fig. 1). Moreover, these data confirm that even in strongly acidic medium, the equilibrium solid phase is not $Ta(OH)_5$ but the compound $Ta(OH)_3(C_2O_4)$. Thus there are no grounds for assuming that the increase in solubility on acidification (curve 3 in Fig. 1) is due to the displacement of $C_2O_4^{2-}$ ions from the coordination sphere of the sparingly soluble complex. This is also confirmed by the data in columns 4, 7, 10, and 13 of Table 1. Thus the increase in solubility in a strongly-acidic medium is described by the equation

$$Ta(OH)_3(C_2O_4) + mH^+ \rightleftharpoons [Ta(OH)_{3-m}(C_2O_4)]^{m+} + mH_2O. \qquad (3)$$
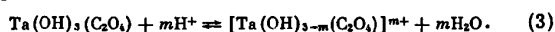
To establish the value of m, we used the data in Fig. 1 to plot the pH dependence of log [Ta], where [Ta] is the

concentration of the soluble complex, that is, the difference between the equilibrium concentration of tantalum and the intrinsic (molecular) solubility of the compound $Ta(OH)_3(C_2O_4)$ (4×10^{-6} M). The result (Fig. 3) shows that increase in the hydrogen ion concentration influences the formation of the soluble complex to the first power, that is, in Eqn. (3) $m = 1$. Using the same data from curve 3 in Fig. 1, we could calculate the constant for the dissociation of the sparingly soluble complex $Ta(OH)_3(C_2O_4)$ to the complex cation $Ta(OH)_2(C_2O_4)^+$ and OH⁻ ions. The concentration of the molecular form of $Ta(OH)_3(C_2O_4)$ in the presence of solid phase is constant and equal to its solubility, 4×10^{-6} M. The concentration of $Ta(OH)_2(C_2O_4)^+$ cations is equal to the difference between the experimentally determined solubility at a given pH and the solubility of the molecular form. The principal data and the calculations are given in Table 2. The mean value of the constant is

$$^{14}k_{3B} = \frac{[Ta(OH)_2(C_2O_4)^+][OH^-]}{[Ta(OH)_3(C_2O_4)]} = (4.7 \pm 0.7) \times 10^{-14}. \qquad (4)$$

The sparingly soluble oxalate $Ta(OH)_3(C_2O_4)$ is stable at pH < 4 (Table 1). The pH at which this compound is converted into tantalum hydroxide is not known, however, and we made a series of experiments on the displacement of $C_2O_4^{2-}$ ions from the inner coordination sphere by OH⁻ ions. Suspensions with a constant quantity of specimen with $Ta : C_2O_4^{2-} = 1 : 1$ were mixed with NH_4OH solutions of

Fig. 3.   Influence of pH on the formation of cationic oxalato-complexes of tantalum (calculated from curve 3 in Fig. 1).
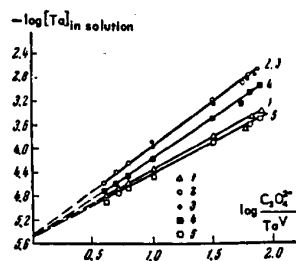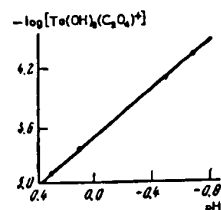
Fig. 2.   Graphical determination of the solubility of the complex with $Ta^V : C_2O_4^{2-} = 1:1$:
1) pH 4;   2) pH 2;   3) pH 1;   4) pH 0;   5) pH 0.3.

TABLE 2.   Calculation of the instability constant of the complex $Ta(OH)_3(C_2O_4)$.

[HNO₃], N	$10^6[Ta]_{total}$, M	$10^6[Ta(OH)_2(C_2O_4)^+]$, M	$10^{14}[OH^-]$	$^{14}k_{3B} = \frac{[Ta(OH)_2(C_2O_4)^+][OH^-]}{[Ta(OH)_3(C_2O_4)]} \times 10^{14}$
0.5	16	12	2.00	6.1
1.0	21	17	1.00	4.3
3.0	58	54	0.33	4.4
5.0	84	80	0.20	4.0

various concentrations, and the acidity was followed potentiometrically. The oxalate concentrations in the precipitate and solution were determined by titration with permanganate, and the tantalum concentration was determined by the reaction with pyrocatechol. The experiments showed that the reaction

$$\underset{\downarrow}{\text{Ta(OH)}_3\,(\text{C}_2\text{O}_4)} + 2\text{OH}^- \rightleftharpoons \text{Ta(OH)}_5 + \text{C}_2\text{O}_4{}^{2-},$$
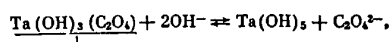
in the absence of an excess of oxalate, takes place at pH 4.2–5.5.

Nature of the Compound Ta(OH)$_3$(C$_2$O$_4$)

The sparingly soluble compound Ta(OH)$_3$(C$_2$O$_4$) may be the oxalate of a cationic hydroxo-complex of tantalum, or the hydroxide of the complex cation Ta(C$_2$O$_4$)$^{3+}$. In the first case it would be expected that the strength (free energy) of the bond formed by tantalum with the OH$^-$ ions would correspond to the strength of the Ta(OH)$_2^{3+}$–OH$^-$ bond. The constant

$$k_s = \frac{[\text{Ta(OH)}_2{}^{3+}][\text{OH}^-]}{[\text{Ta(OH)}_3{}^{2+}]} = 4\times10^{-23},$$

was calculated earlier [1]. This value differs considerably from the value $^{1A}k_{3B} = 4.7 \times 10^{-14}$, which was calculated above [Eqn.(4)], and characterises the strength of the Ta^V–OH$^-$ bond in the monooxalato-compound. In the second case, that is, for the hydroxide of the complex cation Ta(C$_2$O$_4$)$^{3+}$, the strength of the Ta^V–OH$^-$ bond should differ little from that of the same bond in Ta(OH)$_5$. It was previously shown experimentally [1] that

$$k_s = \frac{[\text{Ta(OH)}_4{}^+][\text{OH}^-]}{[\text{Ta(OH)}_5]} = 10\times10^{-14}.$$

Comparison of the values of $^{1A}k_{3B}$ and k_5 shows that the sparingly soluble compound Ta(OH)$_3$(C$_2$O$_4$) should be regarded as the hydroxide of a cationic oxalato-complex of tantalum. Comparison of the values of $^{1A}k_{3B}$ and k_5, together with comparison of curves 2 and 3 in Fig. 1, shows that the basic properties of tantalum hydroxide change little when some of the OH$^-$ ions are replaced by the C$_2$O$_4^{2-}$ ion. Finally, this structure explains the stability of the compound in a strongly acidic medium: as a result of the high strength of the bond in the complex Ta(C$_2$O$_4$)$^{3+}$, acidification leads to the removal of OH$^-$ ions, and not C$_2$O$_4^{2-}$ ions.

Oxalato-Complexes of Tantalum with More Than One Coordinated C$_2$O$_4^{2-}$ Ion

The compound Ta(OH)$_3$(C$_2$O$_4$) dissolves with increase in the oxalic acid concentration (Table 1), due to the formation of tantalum complexes with C$_2$O$_4^{2-}$:Ta > 1. To determine the number of oxalate ions attached on dissolution of the precipitate, we studied the influence of oxalate ion concentration[t] on the formation of the soluble complexes. Comparison of curves 1 and 3 in Fig.1 shows that in the presence of an excess of oxalate we can take as the concentration of the complex with C$_2$O$_4^{2-}$:Ta > 1 the total concentration of tantalum in solution, neglecting the intrinsic solubility of Ta(OH)$_3$(C$_2$O$_4$). In the calculation of the equilibrium concentration of C$_2$O$_4^{2-}$ ions, allowance was made for the

quantity of oxalate combined with tantalum. The data from the calculations are given in Tables 1 and 3, and the logarithmic relationship is given in Fig. 4, which shows that one oxalate ion is added to the insoluble oxalato-complex, that is, in the soluble complex Ta : C$_2$O$_4^{2-}$ = 1 : 2.

To determine the nature of the complex with Ta : C$_2$O$_4^{2-}$ = = 1 : 2 and the equilibrium for its formation, it is important to establish whether the dissolution of Ta(OH)$_3$(C$_2$O$_4$) involves only the attachment of an oxalate ion, or whether displacement of OH$^-$ ions from the coordination sphere of the tantalum also takes place. The data in individual lines in

TABLE 3. Calculation of the instability constants of the complexes.

2 N HNO$_3$ [Ta(OH)$_k$(C$_2$O$_4$)$^+$] = 3.8 × 10^{-8} M			1 N HNO$_3$ [Ta(OH)$_k$(C$_2$O$_4$)$^+$] = 1.9 × 10^{-6} M			0.5 N HNO$_3$ [Ta(OH)$_k$(C$_2$O$_4$)$^+$] = 9.4 × 10^{-6} M		
$10^6[\text{C}_2\text{O}_4^{2-}]$ M	$10^6[\text{Ta}]^{\bullet}$ M	$10^6 k^{\bullet\bullet}$	$10^6[\text{C}_2\text{O}_4^{2-}]$ M	$10^6[\text{Ta}]^{\bullet}$ M	$10^6 k^{\bullet\bullet}$	$10^6[\text{C}_2\text{O}_4^{2-}]$ M	$10^6[\text{Ta}]^{\bullet}$ M	$10^6 k^{\bullet\bullet}$
0.20	0.49	2.1	0.91	0.42	3.9	0.29	1.13	3.5
0.35	0.59	2.2	1.36	0.65	4.0	0.68	1.46	4.3
0.84	1.19	2.7	4.10	1.97	4.0	1.31	4.35	2.9
1.42	1.65	3.2	5.30	3.05	3.3	2.00	4.86	3.9
1.90	2.40	3.0	8.40	4.50	3.5	2.68	9.20	2.8
2.40	3.22	2.8	9.30	6.16	2.9	3.30	11.00	2.9

pH 1 [Ta(OH)$_k$(C$_2$O$_4$)$^+$] = 1.9 × 10^{-6} M			pH 2 [Ta(OH)$_k$(C$_2$O$_4$)$^+$] = 1.9 × 10^{-7} M			pH 4 [Ta(OH)$_k$(C$_2$O$_4$)$^+$] = 1.9 × 10^{-9} M		
$10^6[\text{C}_2\text{O}_4^{2-}]$ M	$10^6[\text{Ta}]^{\bullet}$ M	$10^6 k^{\bullet\bullet\bullet}$	$10^6[\text{C}_2\text{O}_4^{2-}]$ M	$10^6[\text{Ta}]^{\bullet}$ M	$10^6 k^{\bullet\bullet\bullet}$	$10^6[\text{C}_2\text{O}_4^{2-}]$ M	$10^6[\text{Ta}]^{\bullet}$ M	$10^6 k^{\bullet\bullet\bullet}$
0.20	0.60	5.4	0.44	0.63	(13.1)	0.37	0.27	25.8	5.4
0.33	1.55	4.0	0.75	1.18	(11.8)	0.54	0.41	24.6	5.3
0.92	3.47	3.8	1.36	5.52	4.6	1.46	1.28	21.4	4.6
1.40	7.03	3.8	3.04	9.47	6.0	2.22	1.94	21.4	4.6
1.88	9.45	3.7	4.03	13.00	5.9	2.93	2.48	22.5	4.8
2.36	11.30	3.9	5.10	14.60	6.5	3.93	3.24	21.6	4.7

* [Ta] is the concentration of tantalum in the solution, M.

** $k = {}^{2B}k_{2A} = \dfrac{[\text{Ta(OH)}_k(\text{C}_2\text{O}_4)^+][\text{C}_2\text{O}_4^{2-}]}{[\text{Ta(OH)}_k(\text{C}_2\text{O}_4)_2^-]}.$

*** $k = {}^{3B}k_{2A} = \dfrac{[\text{Ta(OH)}_k(\text{C}_2\text{O}_4)^+][\text{C}_2\text{O}_4^{2-}]}{[\text{Ta(OH)}_k(\text{C}_2\text{O}_4)_2^-]}.$
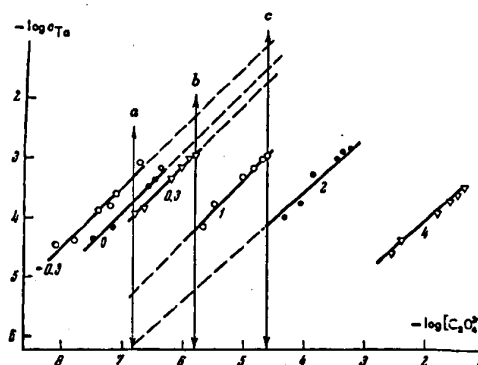

Fig. 4. Determination of the influence of C$_2$O$_4^{2-}$ concentration on the formation of soluble complexes of tantalum. The figures next to the curves give the pH values. Sections *a*, *b*, and *c*: solubility of tantalum complexes at the same C$_2$O$_4^{2-}$ concentrations (see Fig. 5 for significance of symbols used).

[t] In the calculation of the concentration of C$_2$O$_4^{2-}$ ions, we used the values given above for the dissociation constants of oxalic acid.

Table 1 show that at constant total oxalic acid concentration the solubility depends little on the acidity. There are thus no grounds for assuming that the dissolution of $Ta(OH)_3$. $.(C_2O_4)$ involves only the attachment of $C_2O_4^{2-}$ ions with the formation of $Ta(OH)_3(C_2O_4)_2^{2-}$, that is, without the displacement of some of the OH^- ions. In fact, on acidification, for example, from pH 2 to pH 0 (in the presence of a constant excess of oxalic acid), the concentration of free $C_2O_4^{2-}$ ions decreases by a factor of more than 100 (Table 3), whereas the solubility due to formation of the complex decreases to an insignificant extent. This can take place (at constant solid phase composition) only if the formation of the soluble complex involves not only the attachment of $C_2O_4^{2-}$ ions but also the simultaneous displacement of OH^- ions according to the equation

$$Ta(OH)_3(C_2O_4) + nH^+ + C_2O_4^{2-} \rightleftharpoons Ta(OH)_{3-n}(C_2O_4)_2^{(2-n)-} + nH_2O. \quad (5)$$
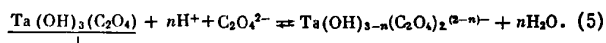
To determine the quantity of OH^- ions displaced, we studied the solubility of tantalum oxalate at constant equilibrium concentration of $C_2O_4^{2-}$ ions (see sections a, b, and c on Fig. 4, and also Fig. 5). It can be seen from Eqn. (5) that the formation of the soluble complex is due to two factors: the increase in acidity and the increase in the concentration of $C_2O_4^{2-}$ ions. Fig. 4 shows the influence of both factors: the straight lines at constant pH characterise the influence of $C_2O_4^{2-}$ ions on the formation of the soluble complexes, and the sections a, b, and c on Fig. 4, together with the data in Fig. 5, show the influence of hydrogen ions on the dissolution of $Ta(OH)_3(C_2O_4)$ (at constant $C_2O_4^{2-}$ ion concentration). The data in Fig. 5 show convincingly that the increase in the H^+ ion concentration (at constant equilibrium concentration of $C_2O_4^{2-}$ ions) is proportional to the increase in the solubility of the oxalate $Ta(OH)_3(C_2O_4)$ to the first power; thus in equilibrium (5) $n = 1$ and Eqn.(5) can be rewritten in the form

$$Ta(OH)_3(C_2O_4) + H^+ + C_2O_4^{2-} \rightleftharpoons Ta(OH)_2(C_2O_4)_2^- + H_2O. \quad (6)$$
solid phase
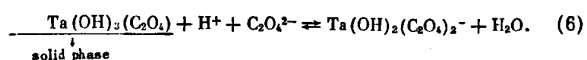
Comparison of the data in Figs. 3 and 5 and Eqns.(3)–(6) shows that, irrespective of whether the system contains an excess of $C_2O_4^{2-}$ ions — Eqns.(5) and (6) — or only a quantity equivalent to the tantalum present — Eqn.(3) — the

ionic forms of tantalum oxalate in strongly acidic solution contain two OH^- groups, that is, the reactions leading to the formation of the soluble complexes involve the ion $Ta(OH)_2^{3+}$ or TaO^{3+}.

Magnitude of the Charge of the Oxalato-Complexes of Tantalum

To confirm that Eqns.(5) and (6) are correct, we determined the magnitude of the charge of the complexes with $Ta : C_2O_4^{2-} = 1:2$. The magnitude of the charge of an anionic complex can be determined[9] from the slope of the curve obtained by plotting the relationship

$$\frac{d \log K_d}{d \log c_A} = \frac{z}{a},$$

where K_d is the distribution constant for the ion being studied, between an anion-exchange resin and solution, c_A the equilibrium concentration of the anion displacing the complex being studied from the anion-exchange resin, and a the magnitude of the charge of this anion. We used as the latter the singly-charged nitrate ion ($a = 1$).

The magnitude of the charge of the oxalato-complex of tantalum formed in 0.5 N HNO_3 was determined by means of the monofunctional, strongly basic, anion-exchange resin Dowex 1 × 2. The solutions, with tantalum concentration 9.2×10^{-4} M, oxalate concentration 8×10^{-3} M, and potassium nitrate concentration from 0 to 2.5 M, were shaken vigorously with weighed portions of the anion-exchange resin until equilibrium was established‡. The concentration of tantalum in the equilibrium solution was determined photometrically; the distribution constant was calculated from the relationship $K_d = [B/(100 - B)](V/m)$, where B is the percentage of tantalum absorbed, V the volume of solution (ml), and m the weight of anion-exchange resin (g). In our case $V = 10$ ml and $m = 0.1$ g.

The results are shown in Figs. 6 and 7 (curve 1). The slope of straight line 1 in Fig.7 shows that $Z = -1$ (tan $\alpha = 1$). These data confirm that in 0.5 N HNO_3 (and, apparently, in other acidic media at pH 4) in the presence of an excess of oxalate, the singly-charged complex $Ta(OH)_2(C_2O_4)_2^-$ is formed.
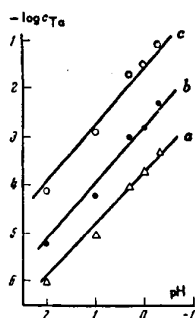

Fig. 5. pH dependence of the formation of soluble complexes of tantalum. The figures next to the curves denote the concentration of free $C_2O_4^{2-}$ ions, M.
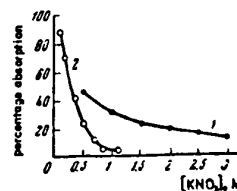

Fig. 6. Displacement of oxalato-complexes of tantalum from an anion-exchange resin with NO_3^- ions: 1) pH 0.3; 2) pH 4.

‡ The anion-exchange resin was first brought into equilibrium with a solution with nitric acid concentration 0.5 N and oxalate concentration 8×10^{-3} M.
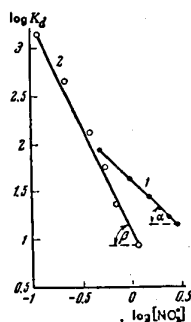
Fig. 7. Determination of the magnitude of the charge of oxalato-complexes of tantalum:
1) pH 0.3, Z = tan α = -1.0; 2) pH = 4,
Z = tan β = -2.2.

Instability Constants of the Complexes

The data obtained can be used to calculate directly the second consecutive instability constant of the complex $Ta(OH)_2(C_2O_4)_2^-$:

$$^{2B}k_{2A} = \frac{[Ta(OH)_2(C_2O_4)^+][C_2O_4^{2-}]}{[Ta(OH)_2(C_2O_4)_2^-]}.$$

The equilibrium concentration of the complex cation $Ta(OH)_2(C_2O_4)^+$ was calculated from the basic dissociation constant of the sparingly soluble tantalum oxalate $Ta(OH)_3$.(C_2O_4) [Eqn. (4)]. In the presence of an excess of oxalate, the concentration of the complex anion $Ta(OH)_2(C_2O_4)_2^-$ is approximately equal to the total concentration of tantalum above the precipitate. The calculation (Table 3) shows that in the range from 2 N HNO₃ to pH 2 the values of the instability constant remain constant, confirming that under these conditions only one complex $Ta(OH)_2(C_2O_4)_2^-$ predominates. The mean value of

$$^{2B}k_{2A} = \frac{[Ta(OH)_2(C_2O_4)^+][C_2O_4^{2-}]}{[TaOH_2(C_2O_4)_2^-]} = (3.8 \pm 0.9) \times 10^{-4}.$$

The first stepwise instability constant of the oxalato-complex of tantalum

$$^{2B}k_{1A} = \frac{[Ta(OH)_2^{3+}][C_2O_4^{2-}]}{[Ta(OH)_2(C_2O_4)^+]},$$

can be calculated from the familiar relationship [10] pk_2/pk_1 = = 0.67 [for the system formed by the triply-charged cation $Ta(OH)_2^{3+}$ with the doubly-charged ligand $C_2O_4^{2-}$]; pk_1 = = 7.41/0.67 = 11.1. Thus

$$^{2B}k_{1A} = \frac{[Ta(OH)_2^{3+}][C_2O_4^{2-}]}{[Ta(OH)_2(C_2O_4)^+]} = 8.0 \times 10^{-12}.$$

The overall instability constant for the complex $Ta(OH)_2$.$(C_2O_4)_2^-$ should be

$$^{2B}K_{2A} = {}^{2B}k_{1A} \times {}^{2B}k_{2A} = 8 \times 10^{-12} \times 3.8 \times 10^{-4} = 3.0 \times 10^{-15}.$$

It can be seen from Table 3 that the instability constant $^{2B}k_{2A}$ at pH 4 differs significantly from that obtained for other pH. Curve 2 in Fig. 7 shows that at pH 4 the complex has a charge of 2-. Thus at pH 4, in Eqns. (5) and (6), n = 0, that is, the soluble complex of tantalum is formed according to the equation

$$\underline{Ta(OH)_3(C_2O_4)} + C_2O_4^{2-} \rightleftarrows Ta(OH)_3(C_2O_4)_2^{3-}.$$
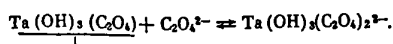
The mean value of the instability constant of this complex (Table 3) is

$$^{3B}k_{2A} = \frac{[Ta(OH)_3(C_2O_4)][C_2O_4^{2-}]}{[Ta(OH)_3(C_2O_4)_2^{3-}]} = (4.9 \pm 0.3) \times 10^{-4}.$$

The difference in the chemistry of formation of the soluble complexes of tantalum at pH 4 and at higher acidities is probably due to the fact that at pH 4 the concentration of the complex cation $Ta(OH)_2(C_2O_4)^+$ — 1.9 × 10⁻⁹ M, see Eqn. (4) — is so small compared with the concentration of $Ta(OH)_3(C_2O_4)_2(4.0 × 10^{-6}$ M), that the attachment of a second $C_2O_4^{2-}$ ion with the formation of the complex $Ta(OH)_2(C_2O_4)_2^-$ is difficult.

We used the value found for the instability constant of the complex $Ta(OH)_2(C_2O_4)_2^-$ to calculate the dependence of the solubility of tantalum hydroxide on pH and the total concentration of oxalic acid in excess. The minimal excess of oxalic acid (Fig. 8) for dissolution of tantalum hydroxide is required at pH 2.5, that is, the oxalato-complex of tantalum is most stable at this pH. The diagram also shows that a 0.1 M solution of tantalum oxalate in an excess of $H_2C_2O_4$ can be prepared only in the pH range 2.0-2.7, since at 20° it is impossible to create $[H_2C_2O_4]$ > > 1 M.

General Characteristics of the Equilibria in the $Ta(OH)_5$-HNO_3-$H_2C_2O_4$ System

The above results lead to certain general conclusions. When $Ta(OH)_5$ is treated with a small excess of oxalic acid, a solid-phase reaction takes place: the sparingly soluble hydroxide salt $Ta(OH)_3(C_2O_4)$ is formed. This solid phase exists over a wide range of acidity from $[H^+]$ > 5 N to pH 4 (Fig. 1 and Table 1). Thus the first stage in the reaction of tantalum with $C_2O_4^{2-}$ ions involves the formation of a sparingly soluble complex compound. Extrapolation to zero concentration of free oxalate showed that in the absence of an excess of oxalic acid, the intrinsic solubility of this compound is 4 × 10⁻⁶ M, which is lower than the solubility of $Ta(OH)_5$ (6 × 10⁻⁶ M).

The solubility of the compound $Ta(OH)_3(C_2O_4)$ is increased in acids. The composition of the solid phase remains constant, but the solubility is always less than the
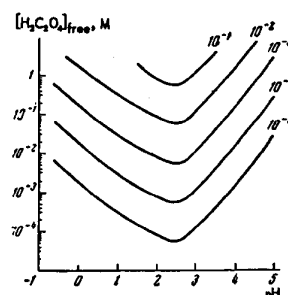

Fig. 8. Dependence of the solubility of tantalum hydroxide on pH and the total oxalate concentration in excess. The figures next to the curves give the total concentration of tantalum in the solution, g-atom litre⁻¹.

solubility of $Ta(OH)_5$ at the same acidity. Thus the increase in solubility in strongly acidic medium is due not to the displacement of $C_2O_4^{2-}$ ions from the solid phase but to the formation of complex cations:

$$Ta(OH)_3(C_2O_4) + H^+ \rightleftarrows Ta(OH)_2(C_2O_4)^+ + H_2O.$$
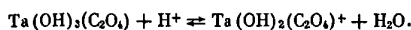
These results are also confirmed by the constant values obtained for

$$^{1A}k_{3B} = \frac{[Ta(OH)_2(C_2O_4)^+][OH^-]}{[Ta(OH)_3(C_2O_4)]} = (4.7 \pm 0.7) \times 10^{-14},$$

in the range 0.5–5 N HNO_3.

This constant characterises the strength of the Ta^V–OH^- bond; comparison with the data for tantalum hydroxide shows that the introduction of the $C_2O_4^{2-}$ ion produces almost no change in the strength of the Ta^V–OH^- bond, that is, the compound $Ta(OH)_3(C_2O_4)$ should be regarded as the hydroxide of the complex cation $Ta(C_2O_4)^{3+}$.

In the presence of an excess of oxalic acid and with decrease in acidity to $[H^+] < 3\,N$, an increase in solubility is observed (Fig. 1), due to the increase in the concentration of free $C_2O_4^{2-}$ ions. Quantitative analysis of the data indicates that the tantalum complex $Ta(OH)_2(C_2O_4)_2^-$ is formed in solution, with instability constant

$$^{2B}k_{2A} = \frac{[Ta(OH)_2(C_2O_4)^+][C_2O_4^{2-}]}{[Ta(OH)_2(C_2O_4)_2^-]} = (3.8 \pm 0.9) \times 10^{-8}.$$

The maximal solubility — in the form of the complex $Ta(OH)_2(C_2O_4)_2^-$ — is reached at pH 2.0–2.5.

The experiments on the determination of the magnitude of the charge of the complexes with $Ta : C_2O_4^{2-} = 1 : 2$ (Fig. 7), together with the calculation of the instability constants of these complexes (Table 3), showed that with further decrease in the acidity to pH $\simeq 4$ the complex $Ta(OH)_2(C_2O_4)_2^-$ in solution is converted into the complex $Ta(OH)_3(C_2O_4)_2^{2-}$. These results can be used to estimate the basic dissociation constant of the complex $Ta(OH)_3(C_2O_4)_2^{2-}$:

$$^{2A}k_{3B} = \frac{[Ta(OH)_2(C_2O_4)_2^-][OH^-]}{[Ta(OH)_3(C_2O_4)_2^{2-}]} \approx 10^{-10}.$$

Comparison of the values of $^{2A}k_{3B}$ and $^{1A}k_{3B}$ shows that the second oxalate ion weakens the Ta^V–OH^- bond.

The decrease in solubility with further increase in pH above 3–4 is due to the fact that this increase in pH does not lead to an increase in the $C_2O_4^{2-}$ concentration, whereas the dissociation of the hydroxide continues to decrease. At pH > 5–6, the solid phase consisting of the hydroxide salt $Ta(OH)_3(C_2O_4)$ is converted into tantalum hydroxide.
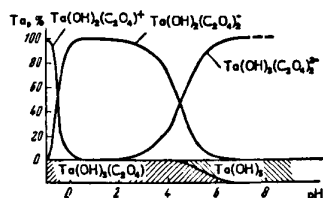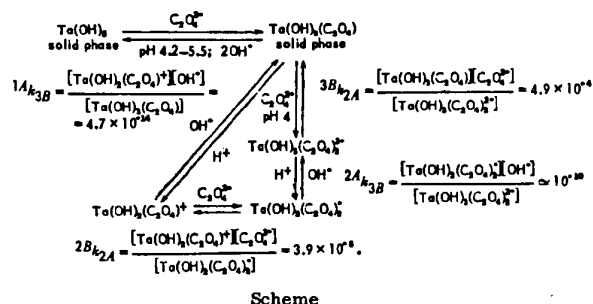

Fig. 9. Distribution of tantalum between different forms in an excess of $H_2C_2O_4$ with concentration 0.1 M. Hatched section: precipitates.

Scheme

A diagram showing the distribution of tantalum between different forms, depending on the pH and the presence of an excess of $H_2C_2O_4$, is shown in Fig. 9, and the interconversion of the different forms is shown in the Scheme. The curves in Fig. 9 were calculated from the instability constants of the complexes $Ta(OH)_2(C_2O_4)_2^-$ and $Ta(OH)_3$. $(C_2O_4)_2^{2-}$ (Table 3) for an excess of $H_2C_2O_4$ with concentration 0.1 M. The calculations show that the position of the distribution curves does not change significantly for other values of the concentration of oxalic acid when in excess.

SUMMARY

Oxalato-complexes of tantalum have been studied by the solubility method. Soluble oxalato-complexes of tantalum are formed in the pH range 0.3–4.3.

The sparingly soluble compound $Ta(OH)_3(C_2O_4)$, with solubility in water equal to 4.0×10^{-6} M, is formed. The constant $^{1A}k_{3B} = \frac{[Ta(OH)_2(C_2O_4)^+][OH^-]}{[Ta(OH)_3(C_2O_4)]} = 4.7 \times 10^{-14}$. In the range from 2 N HNO_3 to pH 2 in the presence of an excess of $H_2C_2O_4$, the singly-charged complex $Ta(OH)_2(C_2O_4)_2^-$ is formed. The second consecutive instability constant of this complex has been calculated: $^{2B}k_{2A} = \frac{[Ta(OH)_2(C_2O_4)^+][C_2O_4^{2-}]}{[Ta(OH)_2(C_2O_4)_2^-]} = (3.9 \pm 0.9) \times 10^{-8}$. The familiar relationships between the consecutive constants have been used to calculate the first consecutive instability constant $^{2B}k_{1A}$ and the cumulative instability constant $^{2B}k_{2A}$ for the complex $Ta(OH)_2$. $(C_2O_4)_2^-$:

$$^{2B}k_{1A} = \frac{[Ta(OH)_2^{2+}][C_2O_4^{2-}]}{[Ta(OH)_2(C_2O_4)^+]} \approx 8.0 \times 10^{-13};$$

$$^{2B}K_{2A} = \frac{[Ta(OH)_2^{2+}][C_2O_4^{2-}]^2}{[Ta(OH)_2(C_2O_4)_2^-]} = {}^{2B}k_{1A} \times {}^{2B}k_{2A} = 3.0 \times 10^{-19}.$$

At pH 4 the complex $Ta(OH)_3(C_2O_4)_2^{2-}$ is formed.

The values of $^{2B}k_{2A}$ for the complex $Ta(OH)_2(C_2O_4)_2^-$ have been used to calculate the dependence of the solubility of tantalum hydroxide on pH and the total concentration of oxalic acid when in excess. The general equilibrium diagram has been examined.

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NIOBIUM AND TANTALUM ARSENITES

I. G. Chufarova and A. K. Sharova

There are few published data on the compounds formed by niobium and tantalum with arsenious acid. Niobium and tantalum arsenites and some of their organic derivatives are used in analysis[1-6]. The present paper describes the conditions for the separation of niobium and tantalum from acid solutions by the action of sodium arsenite, and the determination of the composition and properties of the compounds formed.

EXPERIMENTAL

Starting materials and procedure. Sulphuric acid solutions of niobium and tantalum were prepared from niobium pentoxide containing 99.9% Nb_2O_5 and metallic tantalum containing 99.9% Ta. "Chemically pure" grade sodium arsenite was used. Niobium and tantalum arsenites were precipitated by adding 4% sodium arsenite to sulphuric acid solutions of niobium or tantalum. The original solutions contained Nb_2O_5 1.7, Ta_2O_5 1.1 g litre^{-1}. The precipitates were filtered off after 24 h.

The solutions and precipitates were analysed for niobium by the tannin method, for tantalum colorimetrically with pyrogallol, and for arsenic by titration with bromate. Thermograms were recorded with a photo-recording Kurnakov apparatus. The Debye-Scherrer X-ray diffraction powder method was used.

RESULTS

Precipitation of Niobium and Tantalum from Sulphuric Acid Solutions with Sodium Arsenite

To establish the optimal conditions for the precipitation of niobium and tantalum arsenites from sulphuric acid solutions, we studied the influence of the concentration of sulphuric acid, the quantity of added sodium arsenite, and the temperature and duration of precipitation. The dependence of the degree of precipitation of niobium and tantalum arsenites on the sulphuric acid concentration is shown in Fig. 1 (curves 1 and 3).

With sulphuric acid concentrations of 100-300 g litre^{-1} niobium and tantalum are precipitated almost completely by sodium arsenite. The quantity of niobium and tantalum precipitated decreases with increase in the acidity. With sulphuric acid concentrations of 700-800 g litre^{-1}, niobium remains in solution, whereas ~60% of the tantalum is precipitated. Thus the range of sulphuric acid concentrations in which tantalum arsenite is precipitated is broader than that for niobium. This may be used for preparative purposes to separate niobium and tantalum as their arsenites. Curves 2 and 4 in Fig. 1 illustrate the precipitation of niobium and tantalum with sodium arsenite from solutions heated to 80-90°. Comparison of curves 1 and 2 and curves 3 and 4 shows that heating the solutions does not significantly influence the precipitation of niobium and tantalum arsenites.

The dependence of the degree of precipitation of niobium and tantalum on the quantity of sodium arsenite added to the solution, recalculated as As_2O_3, is shown in Fig. 2. The results indicate that when 0.5% As_2O_3 is added, 74% of the niobium and 94% of the tantalum are precipitated as the arsenites. More complete precipitation requires the
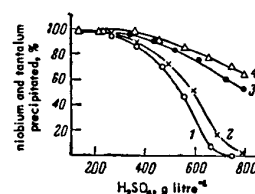

Fig. 1. Influence of sulphuric acid concentration on the degree of precipitation of niobium and tantalum by sodium arsenite. 1), 2) Precipitation of niobium; 3), 4) precipitation of tantalum. 1), 3) At room temperature; 2), 4) at 90°.
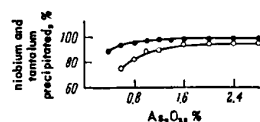

Fig. 2. Influence of the quantity of added sodium arsenite on the degree of precipitation of: 1) niobium; and 2) tantalum.