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Polarographic Catalytic Waves of Titanium(IV) Chelates of EDTA and Related Compounds

Hiroko KANEKO and Takeo OZAWA
Electrotechnical Laboratory, Tanashi, Tokyo

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In the presence of the chlorate ion, the electrode reaction of the various titanium(IV)-chelates is followed by a cyclic process, *i.e.*, an electrochemical reduction of electroactive species generated continuously by coupled chemical oxidation. The reaction rate constant of the regeneration is determined from the ratio of the limiting current observed by the DC polarographic method in the presence of the chlorate ion to that determined without it, and it is calculated using Koutecky's equation. The complex-forming agent decreases the wave height of the catalytic waves of titanium(IV) chelates, and a clear dependency of the height of the catalytic waves on the dissociation constants of the titanium chelates is found. The catalytic wave heights of the titanium(IV) chelates decrease in the order of oxalic acid, NTA, EDTA-OH, EDTA, and CyDTA; the dependency on the stability seems to be the reverse. The logarithm of the dissociation constant is in a linear relation with the logarithm of the catalytic current. The mechanism is discussed on the basis of the above-mentioned facts.

The reduction of titanium(IV) in the presence of the chlorate ion is an example of the type of behavior in which the original depolarizer is regenerated by the reaction of the primary product with a certain component of the solution. These catalytic waves of titanium(IV) in various solutions were investigated.[1–3] The DC polarographic behaviors of the titanium(IV) ion in an ethylenediamine tetraacetate(EDTA)s olution[4] and in a cyclohexanediamine *N*,*N*,*N*′,*N*′-tetraacetate(CyDTA) solution[5] have already been investigated, and the compositions and stability constants of titanium(IV) complexes and the mechanism of the electrode reaction have been determined.

Though it is supposed that, in the presence of a chelating agent, the regeneration rate of titanium(IV) might become considerably slow, no investigation of it has yet been reported. In the present paper, the effects of these EDTA-like agents on the regeneration of titanium(IV) by the chlorate ion are investigated, and the rate constants of the regeneration reactions of some titanium(IV) chelates are calculated by the use of Koutecky's equation.[6] The complex-forming agent decreases the wave height of the catalytic wave of the titanium(IV) chelate, and a clear dependency of the height of the catalytic waves on the dissociation constants of titanium chelates is found.

Experimental

Reagents. All the solutions used were prepared from analytical reagent-grade chemicals. Titanium metal (spongy one) was dissolved in dilute sulfuric acid and oxidized by a small amount of dilute warm nitric acid, after which the solution was standardized by visual chelatometric titration with EDTA as the titrant. The solutions of the complex-forming reagents, EDTA, CyDTA, *N*-(2-hydroxyethyl)-ethylenediamine *N*,*N*′,*N*′-triacetic acid (EDTA-OH), nitrilotriacetic acid (NTA), and oxalic acid (OX), were prepared from commercial analytical-grade chemicals and were standardized by visual titration with a zinc solution and with a Eriochrome Black T solution as the indicator.

Apparatus. Polarographic current-voltage cruves were

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[1] J. Koryta and J. Tenygl, *Collect. Czech. Chem. Commun.*, **19**, 839 (1954).

[2] A. Blazek and J. Koryta, *ibid.*, **18**, 326 (1953).

[3] K. Tanaka, K. Morinaga, and K. Nakano, *Nippon Kagaku Zasshi*, **90**, 478 (1969).

[4] R. L. Pecsok and E. F. Maverick, *J. Amer. Chem. Soc.*, **76**, 358 (1954).

[5] H. Kaneko and K. Kaneko, The Preprint of the symposium on complex salts, Dec. 6 1966, Tokyo.

[6] J. Koutecky, *Collect. Czech. Chem. Commun.*, **18**, 311 (1953).

obtained with a Yanagimoto P8 series polarograph, model P8-DPR. A three-electrode system is utilized in this instrument, and the potentials are measured at intervals of a few seconds with an electrodehammer which also dislodges the mercury drop. The capillary employed for the DME measurements had a capillary constant ($m^{2/3}t^{1/6}$) of 1.14 in 0.1 mol/l sulfuric acid (open circuit), where m is the flow of electrode mercury per second and where t is the drop time.

The pH of the solution was measured immediately after the measurements of the current-voltage curve by means of a Toa HM-5A pH meter equipped with a glass electrode.

Procedure. The measurements were carried out in solutions containing 0.96 mmol/l of titanium(IV), 0.1 mol/l of oxalic aicd, and 0.05 mol/l of potassium chlorate; the concentrations of chelating agents in the solutions were 5, 10, 20, and 50 mmol/l. All the solutions were de-aerated with nitrogen gas for 10 min before the polarogram was obtained. During the course of the measurement, a nitrogen atmosphere was maintained over the solution in the cell. The temperature of the solutions was kept at 25.0°C within a variation of ±0.1°C by using a thermostat. The polarogram of the above-mentioned solution was recorded after recording the wave of the solution of the same composition without potassium chlorate.

Results

The rate constants, k, of the regeneration reactions of some titanium chelates are calculated as follows:

$$\underset{\mathrm{ClO_3^-}}{\mathrm{Ti(IV)}} + \mathrm{e} \longrightarrow \underset{k}{\mathrm{Ti(III)}} \qquad (1)$$

In the case of $i_l/i_d > 2.5$ and $i_l \ll {}_xi_d$, the equation for the total limiting current can be derived from the approximate expression of Koutecky:[6]

$$i_l/i_d = 1 + 0.815\sqrt{kCt} \qquad (2)$$

where i_l and i_d indicate the kinetic current of the catalytic reaction and the diffusion current respectively; where i_l is the sum of i_l and i_d; k, the rate constant of the regeneration reaction of titanium(IV); C, the concentration of the oxidizer; ${}_xi_d$, the hypothetical diffusion current which would be observed for the reduction of all the chlorate ions, and t, the drop time. Equation (2) holds only when the complex-forming agent and the oxidizer exist in a large excess over the titanium(IV) in the solution. In the case of $i_l/i_d > 2.5$, if the relation betwen i_l/i_d and $C^{1/2}$ is linear, the rate of the catalytic reaction of the regeneration of titanium(IV) is rapid and the decrease in the concentration of the oxidizer can be neglected.

When i_l/i_d is plotted against the square root of the concentration of the chlorate ion, the rate constant, k, of the regeneration reaction of titanium(IV) can be obtained from the slopes of these linear plots, provided that the polarographic waves of titanium chelate in the solution without the chlorate ion can be observed. Actually, the polarographic waves of titanium chelates in the solution without the chlorate ion are observed with solutions containing 20 mmol/l of EDTA, EDTA-OH, and CyDTA, 50 mmol/l of NTA, and 0.1 mol/l of oxalic acid respectively at pH 1.

In Fig. 1, the wave height divided by the root of h_0 is plotted against the mercury height, where h_0 is the mercury height corrected for back pressure. It can be inferred that the limiting current of titanium chelate in the solution without the chlorate ion is the diffusion current. This inference is also derived from the temperature coefficient (1.4%/°C) of the wave of the EDTA-OH titanium-chelate (Fig. 9).

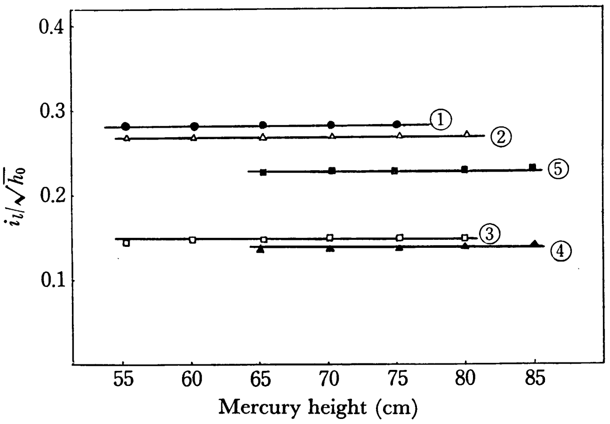

Fig. 1. The effect of mercury height on the diffusion current. 1, OX; 2, NTA; 3, EDTA-OH; 4, EDTA; 5, CyDTA.

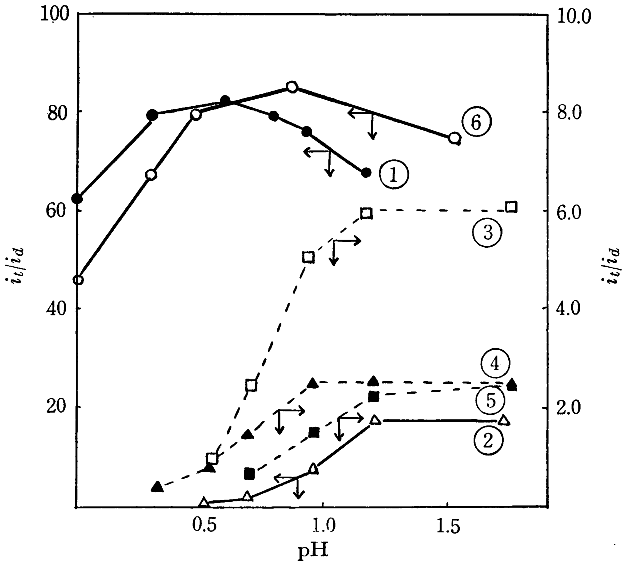

Fig. 2. The effect of pH on i_l/i_d. 1, OX; 2, NTA; 3, EDTA-OH; 4, EDTA; 5, CyDTA; 6, nothing.

Then, the dependencies of the i_l/i_d ratio on the pH of the solution and on the concentration of the chelating agents were observed. In Fig. 2, the dependencies of the i_l/i_d ratio on the pH are shown, where the concentration of the chelating agents is 5 mmol/l, except for oxalic acid and NTA, whose concentrations are 0.1 and 0.02 mol/l. As is shown in Fig. 2, the dependency is negligible in the range of pH larger than 1.2, except for the solution containing oxalic acid and that without any chelating agent. The large variations observed in the latter cases seem to be due to the low stabilities of the complexes. All the measurements hereafter are made by controlling pH within an accuracy of ±0.1. The effect of the pH on the half-wave potential of the catalytic wave is shown in Fig. 3.

The effect of the concentration of the chelating

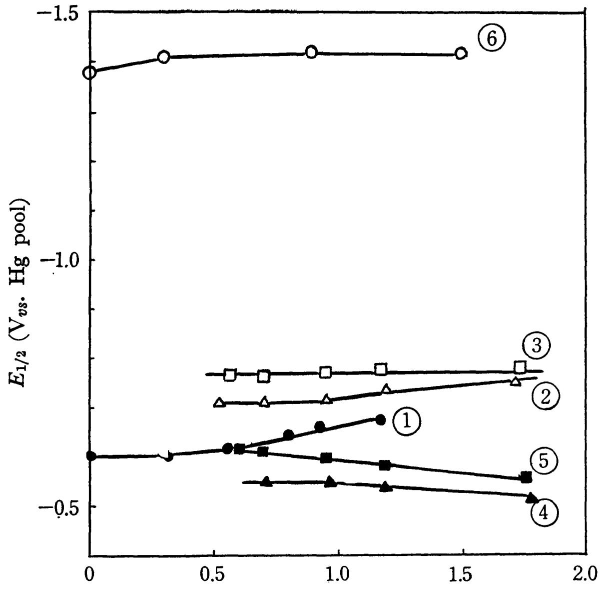

Fig. 3. Effect of pH on half-wave potential. 1, OX; 2, NTA; 3, EDTA-OH; 4, EDTA; 5, CyDTA; 6, nothing.

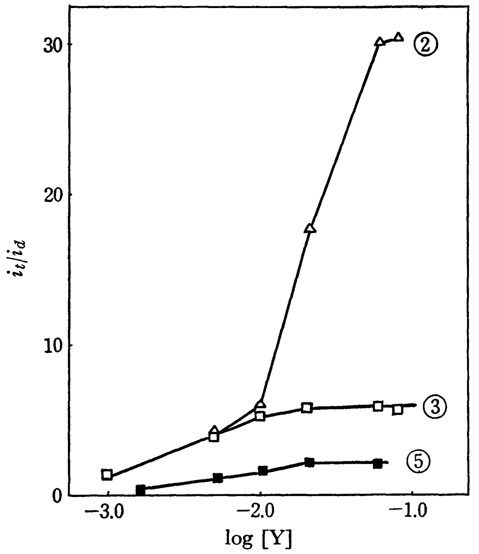

Fig. 4. The effect of the concentration of chelating agents, [Y], on i_t/i_d. 2, OX; 3, EDTA-OH; 5, CyDTA.

agents is shown in Fig. 4, where the concentration of titanium(IV) is 0.94 mmol/l and where that of chlorate is 0.05 mol/l. At concentrations higher than 0.01 mol/l, the dependency of the i_t/i_d ratio on the concentration is low for EDTA-OH and CyDTA; the dependency for EDTA might be similar because its properties are similar to those of CyDTA, while a large dependency is found for the solution containing NTA, where the dependency seems to be negligible for the range higher than 0.05 mol/l and where the precipitation is found in the NTA solution in the range over 0.07 mol/l. This large dependency might be caused by the co-existence of the complex ion containing a single NTA molecule and that complex ions containing NTA molecules. The second wave found for the NTA chelate mentioned below is presumably other evidence of this. Hereafter, the concentration of NTA will be controlled at 0.05 mol/l, and that of oxalic acid at 0.1 mol/l.

The diffusion current of the titanium(IV)-EDTA-OH chelate solution increases as the temperature increases, and its temperature coefficient is 1.4%/°C. However, the catalytic current is in a nonlinear relationship with the temperature (Fig. 5).

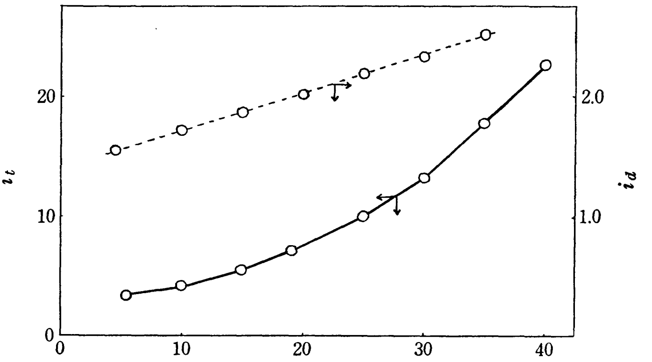

Fig. 5. The effect of the temperature on the diffusion current and the catalytic current of titanium-EDTA-OH complex.

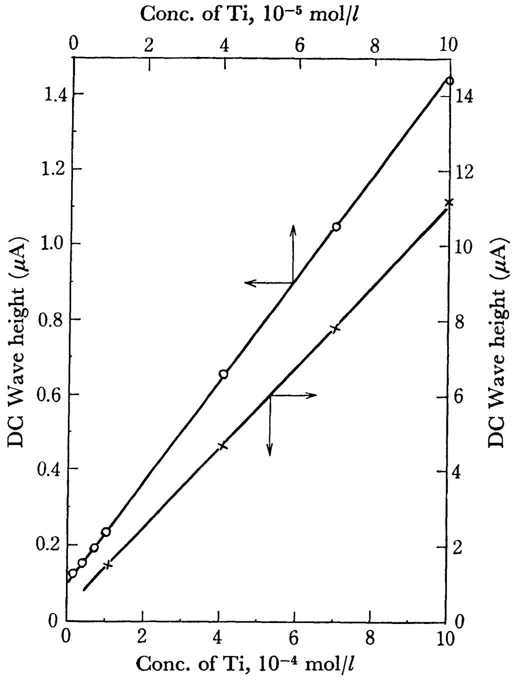

Fig. 6. Calibration curves of the catalytic wave of titanium-EDTA-OH chelate.
pH: 1.2, EDTA-OH: 0.02M, $KClO_3$: 0.05M.

As is shown in Fig. 6, a linear relationship is found between the concentration of titanium(IV)-EDTA-OH and their catalytic current in the presence of 0.05 mol/l potassium chlorate over the range from 1×10^{-6} mol/l, to 1×10^{-3} mol/l of titanium(IV).

In Fig. 7, the values of i_t/i_d at the drop time of 3.0 sec and at pH 1.0±0.1 are plotted against the square root of the concentration of the total chlorate ion. The catalytic wave height of titanium chelates decreases in the order of oxalic acid, NTA, EDTA-OH, EDTA, and CyDTA. Straight lines can be drawn through

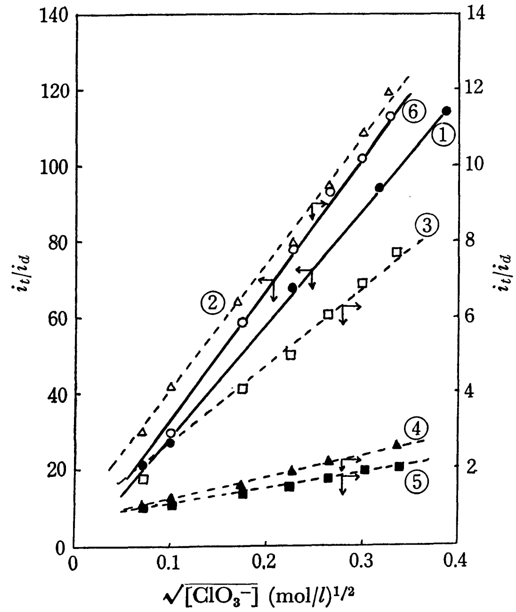

Fig. 7. The catalytic current of the titanium-chelate ion.
1, OX; 2, NTA; 3, EDTA-OH; 4, EDTA; 5, CyDTA; 6, nothing.
Ti: 0.86 mM, pH: 1.0±0.1.

the plots, as is seen in Fig. 7, and the intercepts are 1; these facts are in accordance with Eq. (2). The rate constant of the regeneration can be obtained, since $(i_t/i_d-1)/0.815\sqrt{Ct}$ equals $\sqrt{k}$. The rate constants thus obtained are shown in Figs. 8A and 8B, where the variations in the rate constant with *the drop time* and with *the concentation of the oxidizer* are shown. Here the rate constants, k, in the case of the regeneration of EDTA-Ti(IV) and CyDTA-Ti(IV) are the apparent ones, because the values of i_t/i_d are less than 2.5. As is clearly seen in these figures, there is no variation; these results are in good agreement with Eq. (2). The average values are tabulated in Table 1. For the solution of the titanium-NTA complex, two catalytic waves are observed; the first one is shown in Figs. 7 and 8 and is tabulated in Table 1. Since the values of i_t/h_0 against the mercury height for

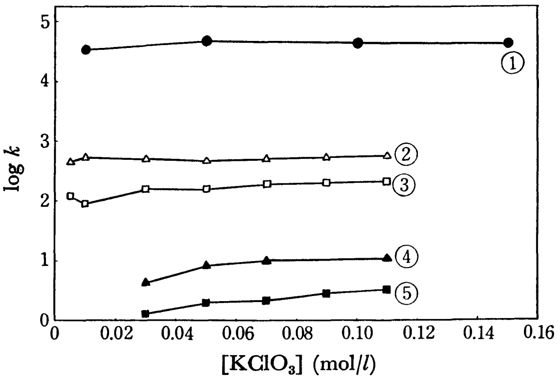

Fig. 8. (A) Relation of log k to the concentration of oxidizer, C.
1, OX; 2, NTA; 3, EDTA-OH; 4, EDTA; 5, CyDTA
Ti: 0.96 mM, H_2SO_4: 0.1M, $KClO_3$: 0.05M.

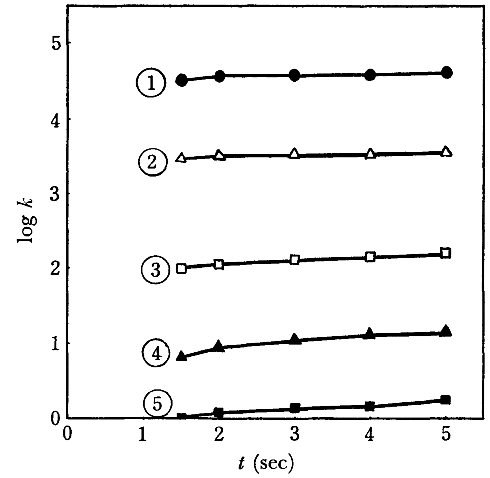

Fig. 8. (B) Relation of log k of drop time t.
1, OX; 2, NTA; 3, EDTA-OH; 4, EDTA; 5, CyDTA
Ti: 0.96 mM, H_2SO_4: 0.1M, t:3.0 sec.

the catalytic wave of 0.96 mmol/l titanium(IV) in 0.1 mol/l sulfuric acid and 0.05 mol/l of potassium chlorate are constant, this wave seems to be controlled by the diffusion of the chlorate ion and to be actually due to the reduction of chlorate ions, catalyzed by the

TABLE 1. POLAROGRAPHIC AND CATALYTIC WAVES OF TITANIUM CHELATES AND THE RATE CONSTANT OF THE REGENERATION OF TITANIUM(IV) CHELATES.

Chelating agents	i_d(μA)	$E_{1/2}$V vs. SCE	$i_t^{a)}$(μA)	i_t/i_d	$E_{1/2}V$ vs. SCE	K l/mol·sec
Nothing	2.05	−0.82	171	82.5	−1.26	6 ×10^4
0.1M OX	2.15	−0.13	162	74.5	−0.32	4.0×10^4
0.1M OX	2.58	−0.30	163.5	62.4	−0.33	
20 mM NTA	1.07	−0.27	21.0	17.5	−0.46	3.3×10^3
50 mM NTA	1.58	−0.27	30.9	18.6	−0.45	
20 mM EDTA-OH	1.83	−0.34	10.5	4.25	−0.47	1.5×10^2
50 mM EDTA-OH	2.14	−0.35	9.9	3.62	−0.48	
20 mM EDTA	2.16	−0.27	4.5	2.5	−0.29	
20 mM CyDTA	1.80	−0.22	2.7	1.1	−0.23	

Ti: 0.96 mM/l, H_2SO_4: 0.1M/l
a) $KClO_3$: 0.05M, pH: 1.0±0.1.
b) In the case of the regeneration reaction of EDTA-titanium chelate and CyDTA-titanium chelate, i_t/i_d is less than 2.5, and the values calculated as the regeneration rate from Eq. (2) are empty.

presence of titanium(IV) ions. Therefore, the rate constant in this case, in Table 1, is the apparent rate constant of the regeneration of titanium(IV), and it seems that the actual rate is more rapid than the apparent one.

On the other hand, the value of k obtained, using 0.1 mol/*l* of oxalate, 0.2 mol/*l* of sulfuric acid, 10^{-3} mol/*l* of titanium chloride, and 0.008—0.256 mol/*l* of potassium chlorate solutions, by Koryta7) is 5.3×10^4 *l*/mol·sec, and that obtained, using 0.2 mol/*l* of oxalate, 3.36 mmol/*l* of the titanium(IV) ion, and 0.06—0.08 mol/*l* of potassium chlorate solutions, by Smith,8) are both 2.5×10^4 *l*/mol·sec. Tanaka *et al.*3) obtained 2.1×10^4 *l*/mol·sec using 0.2 mol/*l* of oxalate, 1×10^{-3} mol/*l* of the titanium(IV) ion, and 0.07—0.15 mol/*l* of sodium chlorate solutions at pH 1.07. The value of k in titanium(IV)-oxalic acid obtained by the present authors is in good agreement with the value obtained by Koryta, though his values are generally somewhat greater than our values, and with those obtained by Smith and by Tanaka *et al.*, though their values are somewhat less than our value. The difference might be caused by the difference in pH and the concentration of the oxalate, as may be seen in Fig. 2.

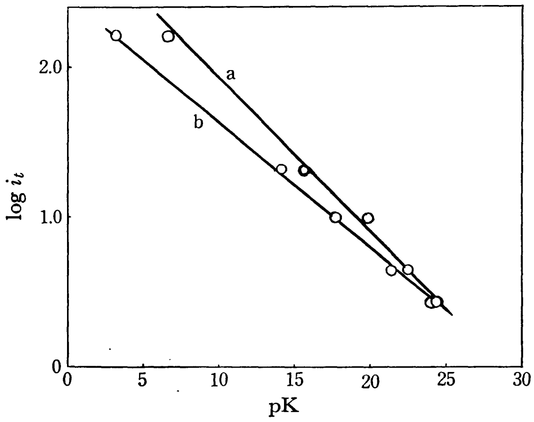

Fig. 9. Relation of $\log i_t$ to $\mathrm{p}K_4$ or $\mathrm{p}K_3$ of the titanium chelates. a is the relation to $\mathrm{p}K_4$ and b to $\mathrm{p}K_3$.
Ti: 0.86 mM, pH: 1.0 ± 0.1, $KClO_3$: 0.05M.
OX: 0.1M, NTA, EDTA-OH: 0.05M, EDTA, CyDTA: 0.02M.

Discussion

As is shown in Figs. 7, 8, and Table 1, the values of i_t/i_d vary according to the kind of chelating agent, and they seem to be in an order the reverse of that of the dependency on the stability of the titanium chelates. In Fig. 9, the i_t values of various titanium (Ti-CyDTA, Ti-EDTA, Ti-EDTA-OH, Ti-NTA, and Ti-OX) are plotted against the logarithms of their stability constants, where the stability constants of titanium-oxalic acid reported by Babco *et al.*,9) of titanium-EDTA reported by Pecsok *et al.*,4) of titanium-CyDTA and titanium-EDTA-OH to be reported elsewhere soon by one of the present authors,5,10) and of titanium-NTA obtained by the same procedure are used. There is a linear relationship between the logarithms of the reciprocal of the dissociation constants and those of catalytic currents of the chelates. The following empirical equation is obtained, by the method of the least squares, between the current and the stability constant of the titanium(III) complex, $\mathrm{p}K_3$.

$$\log i_t = \text{const.} - 0.08\mathrm{p}K_3 \qquad (3)$$

A similar clear linear dependency of the catalytic current on the dissociation constant of the complex of titanium(IV), $\mathrm{p}K_4$, is also found; the empirical equation obtained by the same procedure is as follows.

$$\log i_t = \text{const.} - 0.1\mathrm{p}K_4 \qquad (4)$$

On the other hand, a more simple relationship can be found between the rate constant of the regeneration tabulated in Table 1 and the logarithum of the ratio of the dissociation constant of the titanium(IV) complex to that of the titanium(III) complex; *i.e.*, k is proportional to the logarithms of the ratio of the dissociation constant over the pH range from 1.2 to 1.8 except in the case of oxalic acid. This is shown in Fig. 10(a), as is the empirical equation obtained by using all plots;

$$\log k = -0.1 + 1.4\log K_4/K_3 \qquad (5)$$

where K_4 and K_3 are the dissociation constant of the titanium(IV) complex and that of the titanium(III) complex respectively. Here, the rate constants, k, in the case of the regeneration of EDTA-Ti(IV) and CyDTA-Ti(IV) are the apparent ones because these values of i_t/i_d are less than 2.5.

Thus, the problem to be solved is which one of these three empirical equations is the fundamental one. The confusion is caused by the facts that i_t is roughly proportional to i_t/i_d and that $\log K_4/K_3$ is also in a

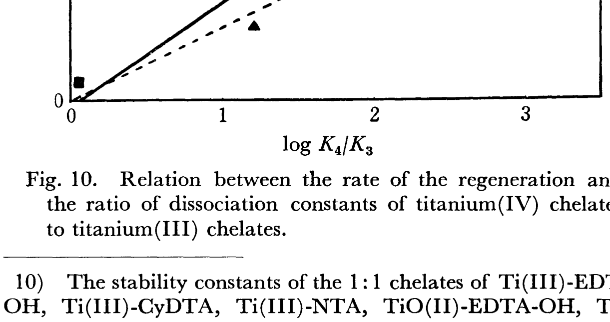

Fig. 10. Relation between the rate of the regeneration and the ratio of dissociation constants of titanium(IV) chelates to titanium(III) chelates.

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7) J. Koryta, *Collect. Czech. Chem. Commun.*, **20**, 1125 (1955).

8) D. Smith, *Anal. Chem.*, **35**, 610 (1963).

9) A. K. Babco and L. I. Dubovenko, *Zh. Neorg. Khim.*, **4**, 372 (1959). L. G. Sillén and A. E. Martell, "Stability constants of Metal ion complexes," The Chemical Society, London (1964), pp. 362, 640.

10) The stability constants of the 1:1 chelates of Ti(III)-EDTA-OH, Ti(III)-CyDTA, Ti(III)-NTA, TiO(II)-EDTA-OH, TiO(II)-CyDTA, and TiO(II)-NTA at pH 1.5 ± 0.1 obtained by one of the present authors are 17.7, 23.8, 13.6, 19.7, 24.3, and 15.4, respectively.

roughly linear relation with pK_4 or pK_3. If Eq. (3) is the true fundamental equation, the mechanism that titanium(III) ions formed by the dissociation of the titanium(III)-chelates are oxidized by the chlorate ions is supported, because the rate of oxidation may depend directly on the concentration of the titanium(III) ion, which in turn depends on the rate of dissociation of the complex, if the dissociation is a rate-determining process, or which, in turn, depends on the stability constant of the complex, if the oxidation is a rate-determining one. This type of effect of the complex is widely observed.[11] However, there are some difficulties in explaining the exponent of 0.08 and the relation of i_t and pK_3. Besides, since the rates of the dissociation of some metal complexes of EDTA and CyDTA are low, they should be in relation not with the stability constants, but with the dissociation rates. The mechanism seems to be implausible.

If the mechanism by which the titanium(III)-chelate complexes are directly oxidized by the chlorate ions is the true mechanism:

$$\begin{array}{ccc} \text{Ti(III)-Y} + \text{Oxid.} & \longrightarrow & \text{Oxid.} \cdots \text{Ti} \cdots \text{Y} \\ & & \downarrow \\ \text{Ti(IV)-Y} + \text{Red.} & \longleftarrow & \text{Red.} \cdots \text{Ti} \cdots \text{Y} \end{array} \tag{6}$$

Equation (5) is directly related to the rule of the linear free energy relation (LFER, Brönsted-Horiuchi-Polanyi-Hammett's rule),[12] since $\log K_4/K_3$ is the difference in the free energies of the product and the reactant of regeneration. As may be seen in Figs. 2 and 4, i_t/i_d depends on the pH and on the concentration of the chelating agents. Hence, the rate constants are also dependent on these parameters. However, except the case of oxalate, the rate constants in Fig. 10 are obtained in the range where i_t/i_d is scarcely dependent on these parameters and where only a single type of complex exists for each chelating agent.[5] On the other hand, it seems that two or more types of complexes, *e.g.*, the complexes with the chelating agent and one with other components of the solution, can exist in the region where i_t/i_d depends on the parameters; therefore, $\log K_4/K_3$ is not equal to the difference in the free energies of the product and the reactant of the regeneration. The scattering of the data in Fig. 10 is caused partly by these effects. As has been mentioned above, since two waves are observed for the NTA complex, there is a possibility of the coexistence of two different type of complexes. The first wave may be due to the complex of titanium with a single molecule of NTA, while K_3 and K_4 are apparent equilibrium constants among two more types of complexes. Therefore, there are some questions of including the plot of the NTA complex, and also of including the plot of the oxalate complex for the reason mentioned above. If we omit their two plots, a less-scattered relation can be obtained, as is shown by Line(b) in Fig. 10(b), and the empirical equation is:

$$\log k = -0.05 + 1.0 \log K_4/K_3 \tag{7}$$

The relation is very clear and simple, the mechanism is in accordance with the postulation of Vlcek,[13] and a similar mechanism has also been reported for other complexes.[14] However, K_4 is not the dissociation constant of the titanim(IV) complex but that of the titanyl complex. The process of the oxidation of the titanium(III) complex consists of the process of the oxidation of the titanium(III) ion and the hydrolysis of the titanium(IV) ion to the titanyl ion, and the rate of oxidation observed may be that of the titanium(III) complex to the titanyl complex.

Since the reactions are complicated, no conclusion supported by clear, direct evidence can be obtained, but the mechanism would be elucidated if similar reactions were observed for other ion-complexes.

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[11] A. E. Martell and M. Calvin, "Chemistry of the metal chelate compounds," Prentice-Hall, Englewood Cliffs (1956).

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[13] A. A. Vlcek, "Progress in Inorganic Chemistry," Vol. 5, ed. by F. A. Cotton, Interscience Publishers, New York, London, Sydny (1967) p. 326.

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