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The Peroxo Complexes of Titanium

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The formation of homogeneous solutions of peroxotitanium was achieved without adding any excess of acid by starting from pure $TiCl_4$ and concentrated H_2O_2. This allowed the determination of the number of hydrogen ions n which are liberated in the process $Ti \cdot aq^{4+} + H_2O_2 \rightarrow Ti(O_2)(OH)_{n-2}{}^{4-n+} + nH^+$. Below pH 1 the complex formed has a single charge per metal and probably is mononuclear: $Ti(O_2)OH \cdot aq^+$. Above pH 1 condensation takes place to various deprotonation products of dinuclear $Ti_2O_5 \cdot aq^{2+}$. The primarily formed species $Ti_2O_5(OH)_x{}^{2-x}$, with $x = 1$–6, were studied in a rapid-flow apparatus. They slowly condense to polynuclear cations and anions (depending on x), and finally a precipitate of peroxotitanium hydrate $TiO_3(OH_2)_{1(2)}$ is obtained. Chelates of mononuclear $TiO_2{}^{2+}$ as well as of dinuclear $Ti_2O_5{}^{2+}$ are produced, depending on the acidity of the mixtures and the dentation of the chelating ligand. Crystallized complex salts were obtained with dipicolinic acid, nitrilotriacetic acid, and EDTA and are the first peroxotitanium compounds which are suitable for X-ray investigation.

The appearance of an intense orange color on addition of H_2O_2 to an acidic solution of Ti(IV) was noted for the first time just a century ago.[1] A considerable number of papers describe the analytical application of this reaction for the detection or photometric determination of either titanium or hydrogen peroxide. In spite of the analytical importance, however, remarkably little has been established positively about the compounds produced.

It seems to have been impossible to isolate the products in the form of well-defined, crystalline compounds. Amorphous sulfates of approximate stoichiometric compositions $Ti(O_2)SO_4 \cdot 3H_2O$[2] and $K_2SO_4 \cdot Ti(O_2)SO_4 \cdot 3H_2O$[3] have been obtained by precipitation with ethanol. Corresponding amorphous peroxotitanium oxalates, malonates, and maleinates have also been described.[4] Moderately acid solutions (pH >2) slowly deposit an amorphous precipitate of peroxotitanium hydrate $TiO_3(H_2O)_x$, which can be obtained more quickly by adding a base. The existence of one peroxo group $O_2{}^{2-}$ per titanium has been established by analysis, but there was some discussion as to the number of water molecules (x), *viz.*, $x = 1$ ($Ti(O_2)(OH)_2$)[5-7] or $x = 2$.[8,9] Adding ammonium fluoride and NH_3 precipitates a yellow solid $(NH_4)_3Ti(O_2)F_5$,[10] which is the only crystalline compound obtained so far. In all of these preparations the ratio of peroxo groups to titanium is 1:1. Compounds with higher ratios can be obtained only from strongly alkaline solutions.[8,11,12]

The species produced in solution also contain one peroxo group per metal, as has been shown unambiguously by photometric studies.[11,13-16] The color of these solutions is orange below pH 1, is yellow around pH 3, becomes pale yellow when the pH is raised further, and disappears in the alkaline region. The absorption spectra indicate the presence of a definite species below pH 1, there being no further changes in the spectra at still higher acidities.[11,13,14,17] Electromigration and dialysis studies[18] show it to be a cationic complex, the spectrum of which is not influenced by the presence of simple anions such as HSO_4^-, NO_3^-, ClO_4^-, Cl^-.[15] If this species is assumed to be mononuclear, the formula can be denoted by $Ti(O_2)(OH)_{n-2}{}^{(4-n)+}$. When the pH is increased, this ion will lose protons from the water molecules, which complete the coordination of the metal ion, thus increasing n and causing the color

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(1) G. Schönn, *Z. Anal. Chem.*, **9**, 41 (1870).

(2) C. C. Patel and M. Mohan, *Nature (London)*, **186**, 803 (1960).

(3) R. Schwarz, *Z. Anorg. Allg. Chem.*, **210**, 303 (1933).

(4) G. V. Jere and C. C. Patel, *Nature (London)*, **194**, 471 (1962).

(5) F. Fichter and A. Goldach *Helv. Chim. Acta*, **13**, 1200 (1930).

(6) G. V. Jere and C. C. Patel, *Z. Anorg. Allg. Chem.*, **319**, 175 (1962).

(7) F. Riveng, *Bull. Soc. Chim. Fr.*, (5) **12**, 283 (1945).

(8) R. Schwarz and H. Giese, *Z. Anorg. Allg. Chem.*, **176**, 209 (1928).

(9) M. Schenk, *Helv. Chim. Acta*, **19**, 625 (1936).

(10) A. Piccini, *C. R. Acad. Sci.*, **97**, 1064 (1883); *Gazz. Chim. Ital.*, **17**, 479 (1887); *Z. Anorg. Allg. Chem.*, **10**, 438 (1895).

(11) M. Mori, N. Shibata, E. Kyono, and S. Ito, *Bull. Chem. Soc. Jap.*, **29**, 904 (1956).

(12) P. Melikov and L. Pissarevski, *Chem. Ber.*, **31**, 953 (1898).

(13) A. K. Babko and N. V. Ul'ko, *Ukr. Khim. Zh.*, **27**, 101 (1961).

(14) A. K. Babko and A. I. Volkova, *Zh. Obshch. Khim.*, **21**, 1949 (1951).

(15) E. Gastinger, *Z. Anorg. Allg. Chem.*, **275**, 331 (1954).

(16) Y. Schäppi and W. D. Treadwell, *Helv. Chim. Acta*, **31**, 577 (1948).

(17) A. K. Babko, A. I. Volkova, and S. L. Lisichenok, *Russ. J. Inorg. Chem.*, **11**, 260 (1966).

(18) K. F. Jahr, *FIAT Rev. Ger. Sci.*, **3**, 170 (1948).

changes. However, the *n* value of the species existing in solution below pH 1 is not known and different authors disagree widely, suggesting $Ti(H_2O_2)^{4+}$ ($n = 0$)[13] or $Ti(O_2)^{2+}$ ($n = 2$)[10,19] for its composition.

1. The Complex of Strongly Acidic Solutions.—The value *n* denotes the number of hydrogen ions which are liberated when the peroxo complex is produced from the titanium–aquo ion and H_2O_2 which may be added in any excess

$$Ti^{4+}(aq) + H_2O_2 \longrightarrow Ti(O_2)(OH)_{n-2}{}^{4-n+} + nH^+ \qquad (1)$$

However, the existence of the simple aquotitanium cation $Ti(OH_2)_n{}^{4+}$ is doubtful, and it certainly does not occur above pH ∼0. Titanium chloride and titanyl sulfate are hydrolyzed immediately in water, resulting in turbid solutions which can be made homogeneous only by adding a large excess of mineral acid, thus making the determination of the number of hydrogen ions produced by adding H_2O_2 (process 1) impossible.

However, the following procedure proved to be practicable. When at low temperature (−30°) pure liquid titanium chloride is introduced in an approximately eutectic mixture of H_2O_2 and H_2O (which does not solidify above −40°), the droplets of $TiCl_4$, disintegrated by the stirrer, dissolve slowly yielding a deep red homogeneous solution. Our standard solution A was obtained through dilution and had the following composition: total titanium, $[Ti]_t = 0.1$; total peroxide, $[H_2O_2]_t = 1$; chloride, $[Cl^-] = 0.4$; acidity, $[H^+] = 0.1n = ?$.

The number of hydrogen ions produced by reaction 1 is at least $n = 1$; thus solution A has a pH of 1 or below and all the titanium exists in the form of the definite species with the pH-independent absorption spectrum mentioned above. The value *n*, therefore, should be an integer which can be determined by measuring the concentration $[H^+]$.

The accurate potentiometric determination of the hydrogen ion concentration of a strongly acidic solution cannot be carried out like a conventional pH measurement because of the large diffusion potentials occurring at the liquid–liquid boundary to the medium containing the reference electrode. We have used the following galvanic cells

(I) glass electrode | solution A | solution R | AgCl, Ag — potential E_1

(II) glass electrode | solution R | AgCl, Ag — potential E_2

Composition of the reference solution R is as follows: [HCl] = *c*; [KCl] = 0.4 − *c*. The solution R containing the reference electrode had therefore the same chloride concentration as solution A, and the positive ions H^+ and K^+ were present in varying ratios (*c* = 0.1, 0.2, 0.3, 0.4). The potentials E_1 and E_2 were measured with the same glass electrode immersed in the case of system I, into the solution A and in the case of system II, into the reference solution R. Cell II does not include a liquid–liquid junction, and the difference $(E_1 - E_2)$ is therefore the same as the potential of the galvanic cell III determined with two exactly identical glass electrodes.

$$\text{(III)}\quad \text{glass} \mid \text{solution A} \left| \begin{matrix} c\ M\ \text{HCl} \\ (0.4 - c)\ M\ \text{KCl} \end{matrix} \right| \text{glass} \qquad \text{potential } (E_1 - E_2)$$

$(E_1 - E_2)$ is positive if solution A is more acidic than R and *vice versa*, but its absolute value will be smaller than 58 log $\{[H]_A/[H]_R\}$ mV, because of the considerable potential at the phase boundary of the two liquids of different acidity. When the hydrogen ion concentrations of A and R are identical, $(E_1 - E_2)$ will be small although not exactly zero, because of small differences in the activity coefficients of the ion H^+ in the two solutions and a still existing junction potential of small magnitude. The following potentials were measured

c, *M*	0.1	0.2	0.3	0.4
$(E_1 - E_2)$, mV	+14.5	+3.5	+0.7	−2.2

Because the number *n* (= $[H]_A/0.1$) must be an integer, the result is unequivocal: $[H]_A = 0.3$ and $n = 3$. This fixes the stoichiometry of the orange-red compound formed in very acidic solutions. Assuming a mononuclear complex, its formula is $Ti(O_2)OH^+$.

2. Neutralization and Hydrolysis.—The color of solution A changes to yellow on dilution and disappears on neutralization. A titration with NaOH carried out at a total metal concentration $[Ti]_t = 5 \times 10^{-3}\ M$ after adding $NaClO_4$ in order to create an ionic strength $\mu = 0.1$ yielded the curve of Figure 1. The degree of neutralization $\bar{n}$ is obtained with eq 2 from the number of moles of base added per titanium (*a*).

$$\bar{n} = a + \frac{[H^+] - [OH^-] - [HO_2^-]}{[Ti]_t} \qquad (2)$$

Unfortunately, the curve of Figure 1 cannot be analyzed mathematically since it had to be obtained rapidly, within a few minutes with an automatic titrator, so that the equilibria were not established. Hydrolytic processes prevented a normal titration. The hydrolysis is quite slow below pH 3, but even in these acidic solutions,

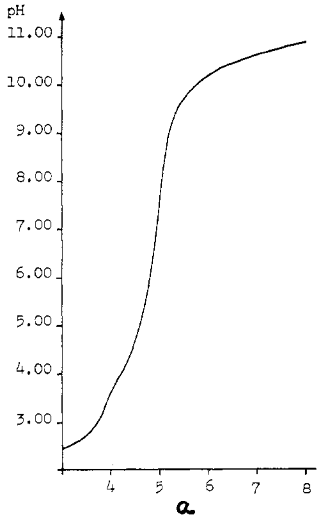

Figure 1.—Alkalimetric titration of standard solution A diluted to $[Ti]_t = 5 \times 10^{-3}\ M$, $[H_2O_2] = 5 \times 10^{-2}\ M$, and $\mu = 0.1$ ($NaClO_4$) without any further addition.

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(19) R. Viallet, *C. R. Acad. Sci.*, **252**, 1789 (1961).

condensation reactions are going on, so that the solutions turn turbid after 1 or 2 days, depositing slowly a precipitate of yellow amorphous peroxotitanium hydrate $TiO_3(H_2O)_x$. The solutions become less stable the higher the pH. As long as the $\bar{n}$ values are smaller than 4, the condensation reaction is accompanied by a pH drop, but at $\bar{n} > 4$ by a pH rise. It is evident that this is due to the condensation of cationic peroxo species to the uncharged $TiO_3 \cdot aq$ producing H^+ ($\bar{n} < 4$), and the condensation of anionic species producing OH^- ($\bar{n} > 4$).

Although it is impossible to analyze the curve of Figure 1 quantitatively, it tells us that the value $\bar{n} = 4$ is reached at pH 3. This means that the solution contains at this pH an uncharged complex $TiO_2(OH)_2$ or its condensation products $[TiO_2O]_q \cdot aq$. However, the $\bar{n}$ value can be raised above 4 by neutralizing the solutions further, thus forming anionic peroxotitanium species. At pH 7, $\bar{n} = 5$ is reached, corresponding to the mononuclear complex $Ti(O_2)(OH)_3^-$. As mentioned, these solutions are unstable, and the condensation, leading eventually again to the precipitate $TiO_3 \cdot aq$, is accompanied now by a pH rise and a decrease of $\bar{n}$ on standing (compare eq 2).

3. Deprotonation in the Range 1 < pH < 3.—The deprotonation between pH 1 and 3 which increases $\bar{n}$ from 3 to 4 is accompanied by a color change and can be studied spectrophotometrically. The condensation to polynuclear species is quite slow in this range and without influence at times not more than a few minutes. Solution A was diluted 100 times to $[Ti]_t = 10^{-3}$ *M* with buffers containing KCl and HCl (in a few cases NaOH), so that all the mixtures (solutions B) had an ionic strength of $\mu = 0.1$ and a definite pH. The absorption spectra were taken immediately after preparing the solutions using the Cary 14 spectrophotometer.

From the results (Figure 2) it becomes apparent that the increase of $\bar{n}$ from 3 to 4 cannot be simply due to the deprotonation of the mononuclear $Ti(O_2)OH^+$ and to the formation of $Ti(O_2)(OH)_2$. The absence of isosbestic points indicates that the solutions contain at least three absorbing species and we can assume either that all of these are dinuclear (case 3.1) or that condensation takes place only when the acidity is lowered (case 3.2).

3.1. When already the definite species existing below pH 1 is dinuclear, its formula would be $[Ti(O_2)OH]_2^{2+}$ which can be written as $Ti_2O_5 \cdot aq^{2+}$ (I). On raising the pH a simple deprotonation of coordinated water produces II and III.

$$\underset{\mathrm{I}}{Ti_2O_5^{2+}} \rightleftharpoons \underset{\mathrm{II}}{Ti_2O_5(OH)^+} \rightleftharpoons \underset{\mathrm{III}}{Ti_2O_5(OH)_2} \qquad (3)$$

The optical density $[D = (1/d) \log (I_0/I)]$ is given by eq 5 containing the molar extinction coefficients ϵ_I, ϵ_{II}, ϵ_{III} of the three colored species as well as the acidity constants pK_1 and pK_2 of the proton donators defined by eq 4.

$$\beta_1 = 10^{pK_1} = \frac{[Ti_2O_5]}{[H][Ti_2O_5OH]}$$

$$\beta_2 = 10^{pK_1+pK_2} = \frac{[Ti_2O_5]}{[H]^2[Ti_2O_5(OH)_2]} \qquad (4)$$

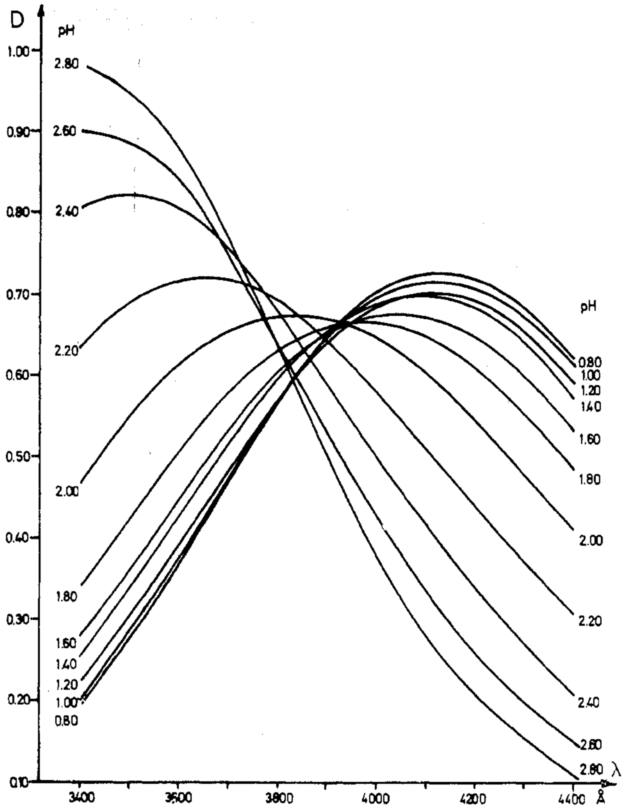


Figure 2.—Spectra of standard solution A diluted to $[Ti] = 10^{-3}$ *M* and $[H_2O_2] = 10^{-2}$ *M* with pH varying from 1 to 3 and constant $\mu = 0.1$ made up with HCl and KCl.

$$D = {}^1/_2[Ti]_t \frac{\epsilon_I + \epsilon_{II}\beta_1[H] + \epsilon_{III}\beta_2[H]^2}{1 + \beta_1[H] + \beta_2[H[^2} \qquad (5)$$

Only ϵ_I can be determined directly with a solution containing all the Ti as $Ti_2O_5^{2+}$ (pH <1). The other four parameters (ϵ_{II}, ϵ_{III}, β_1, β_2) must be treated as unknowns. Using a computer program by Professor G. Anderegg, a fairly good fit with the spectra of Figure 2 was obtained furnishing the acidity constants $pK_1 = 2.53$ and $pK_2 = 2.05$. It is noteworthy that pK_1 is larger than pK_2 and that the intermediate II therefore has only a small range of existence, its maximum concentration at pH ${}^1/_2(pK_1 + pK_2)$ being only 22% of $[Ti_2O_5]_t = {}^1/_2[Ti]_t$. It is not often found that the loss of a proton gives rise to the production of a stronger acid than the starting material.

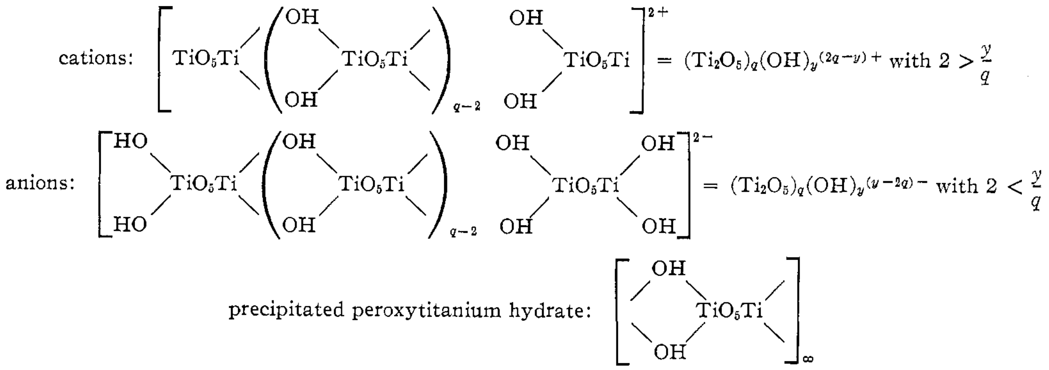
3.2. We consider it therefore as more likely that the definite peroxotitanium present below pH 1 is mononuclear and that condensation to a dinuclear complex (eq 6) takes place when the acidity is lowered.

$$\underset{\mathrm{I}}{2Ti(O_2)OH^+} \rightleftharpoons \underset{\mathrm{II}}{Ti_2O_5(OH)^+} \rightleftharpoons \underset{\mathrm{III}}{Ti_2O_5(OH)_2} \qquad (6)$$

In order to distinguish between (3) and (6) more accurate photometric measurements would have to be carried out on solutions containing different metal concentrations $[Ti]_t$.

4. Rapid Neutralization in the Range 3 < pH < 9.—As demonstrated in section 2, the $\bar{n}$ value rises above 4 when the peroxotitanium solution is titrated with alkali metal hydroxide implying the formation of anionic

CHART I



species. If no further condensation takes place, these species must be dinuclear and are formed by deprotonation of the water molecules coordinated to the metal atoms of the central group $Ti_2O_5^{2+}$. The general formula $Ti_2O_5(OH)_x^{(2-x)+}$ therefore is appropriate for these products.

All of these complexes, however, condense to polynuclears and the precipitate of peroxotitanium hydrate ($TiO_3\cdot aq$) is finally obtained. These processes may be formulated with (7) and (8), depending on whether x is smaller or larger than 2.

$$x < 2:\quad Ti_2O_5(OH)_x^{(2-x)+} \xrightarrow{H_2O} \frac{1}{q}(Ti_2O_5)_q(OH)_y^{(2q-y)+} + ((y/q) - x)H^+ \longrightarrow 2TiO_3\cdot aq + (2 - x)H^+ \tag{7}$$

$$x > 2:\quad Ti_2O_5(OH)_x^{(x-2)-} \longrightarrow \frac{1}{q}(Ti_2O_5)_q(OH)_y^{(y-2q)-} + (x - (y/q))OH^- \longrightarrow 2TiO_3\cdot aq + (x - 2)OH^- \tag{8}$$

Below pH 3, x is smaller than 2, the condensing complexes are cations or uncharged $Ti_2O_5(OH)_2$, and the primarily formed lower polynuclears of the still homogeneous solutions must also be positively charged ($2 > y/q > x$). In this range the reaction—which is accompanied by a pH drop—is slow, which made the optical investigation of the deprotonation up to $x = 2$ possible (reaction 3 or 6, section 3).

Above pH 3, x is larger than 2, the condensing species are anions or $Ti_2O_5(OH)_2$, and the precursors of the final precipitate must also be negatively charged polymers ($2 < y/q < x$). The rate of condensation—which is accompanied by a pH rise—is now much faster and speeds up with increasing pH.

It is reasonable to assume that the units $Ti_2O_5(OH)_2$ will condense by forming μ-hydroxy bridges between the metal atoms as illustrated by the formulas shown in Chart I.

Coordinated water has been omitted from these formulas. If each Ti carries such a molecule of H_2O, the composition of the peroxytitanium hydrate is $TiO_3\cdot 1.5H_2O$ which is about what has been found analytically.[8]

Although the rate of condensation is rather large in the pH range 3–9, it is by no means instantaneous. The solutions remain clear for quite a while after adding the base and in an automatic titrator (Figure 1) the $\bar{n}$ value can be raised well up to 5. The condensation proved to be sufficiently slow over the whole pH range to permit a study of the deprotonation of the dinuclear $Ti_2O_5\cdot aq^{2+}$ by rapid alkalization.

The proton-transfer reactions between $Ti_2O_5^{2+}$ and OH^- must come to equilibrium in a few microseconds, so that there should be ample time to study these equilibria by measuring the pH of the mixtures before the condensation reactions become significant. This has been accomplished with a streaming device[20] which allows the mixing of the acidic solution containing the peroxotitanium and the solution of NaOH, as well as the determination of the pH of the fresh mixture within about 5 msec. The instrument allows a second pH measurement to be made about 10 msec after mixing. It was found that the pH does not change within this short time, thus proving that we are dealing with a true preequilibrium which can only be due to the simple protolytic processes

$$Ti_2O_5(OH)_2 \underset{pK_3}{\rightleftharpoons} Ti_2O_5(OH)_3^- \underset{pK_4}{\rightleftharpoons} Ti_2O_5(OH)_4^{2-} \underset{pK_5}{\rightleftharpoons} \text{etc.} \tag{9}$$

However, in a rapidly streaming solution, the pH cannot be determined as accurately as in a solution at rest. This must be taken into account when the results presented in Figure 3 are evaluated. One of the two pressure vessels of the streaming apparatus was filled with the standard solution A, the other with NaOH in a concentration yielding a definite degree of neutralization "a" on mixing. In the course of the experiment, both solutions were first diluted in dilution chambers with a solvent containing the inert electrolyte KCl and some H_2O_2; the diluted solutions then streamed into the mixing chamber, whence the mixture passed the glass electrode. From the pH, $\bar{n}$ was calculated with eq 2. The concentrations in the mixing chamber were $[Ti]_t = 3.5 \times 10^{-3}\ M$, $[H_2O_2]_t = 0.1\ M$, $\mu = 0.1$ (KCl). The precision of the pH is about ±0.05 unit giving an appreciable error in $\bar{n}$ for pH values below 4. (Solutions containing H_2O_2 are usually supersaturated with O_2. Thus small bubbles were often formed in the narrow tubings which influenced the hydrodynamic behavior of the streaming liquids unfavorably.)

In spite of these inaccuracies, Figure 3 demonstrates definitely that the peroxotitanium complex can be

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[20] G. Schwarzenbach, *Pure Appl. Chem.*, **5**, 377 (1962).

deprotonated up to an $\bar{n}$ value of at least 6, corresponding to the dinuclear complex of the formula $Ti_2O_5(OH)_6^{4-}$. (At still higher ratios of NaOH per titanium, the mixtures became very unstable and the pH values uncertain. The results of these experiments are not presented.)

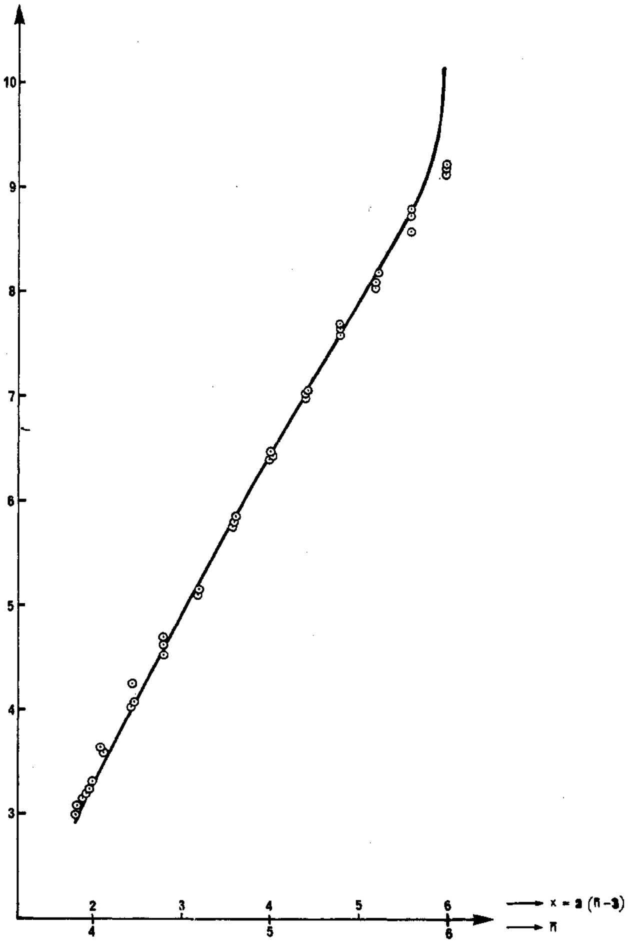

Figure 3.—Rapid alkalization of peroxotitanium obtained with the flow apparatus. The pressure vessels contained standard solution A and NaOH (concentration 0.3 → 0.6 M), respectively. During the measurement these solutions are injected separately into a stream of the solvent containing the inert electrolyte (KCl) and some H_2O_2. The diluted solutions finally are mixed in the mixing chamber where the analytical concentrations were as follows: $[Ti]_t = 3.53 \times 10^{-3}\ M$, $[H_2O_2] = 0.1\ M$, $\mu = 0.1$ (KCl). The line has been computed with eq 11.

As shown in Figure 3, the pH rises almost linearly with $\bar{n}$ between pH 3.5 and 9.2, corresponding to the range $4 < \bar{n} < 6$. A mononuclear complex $Ti(O_2)(OH)_2$ (corresponding to $\bar{n} = 4$) would have only two buffer regions in this $\bar{n}$ range. However, the linear rise of pH with $\bar{n}$ can well be explained with the dinuclear species $Ti_2O_5(OH)_x$; while x increases from 2 to 6 in the formation of $Ti_2O_5(OH)_6^{4-}$ ($n = 6$), we get four strongly overlapping buffer regions. With four pK values, more or less evenly spaced, the course of the experimentally obtained neutralization curve is readily interpreted, thus supporting the evidence for dinuclear peroxotitanium complexes.

The curve drawn through the experimental points in Figure 3 was computed with eq 11, using the following pK_x values: $pK_3 = 4.1$, $pK_4 = 5.6$, $pK_5 = 7.2$, $pK_6 = 8.5$. The index number corresponds to the x in the formula $Ti_2O_5(OH)_x^{(2-x)+}$. The definition of pK_1 is given with eq 4 and the others are defined analogously

$$pK_x = \log \frac{[Ti_2O_5(OH)_{x-1}]}{[H^+][Ti_2O_5(OH)_x]} \tag{10}$$

$$\bar{x} + \sum_{x=0}^{6} (\bar{x} - x) \times 10^{x\text{pH} - \sum_{x=1}^{x} pK_x} = 0$$
$$[\bar{x} = 2(\bar{n} - 3) \text{ and } x = 1\text{–}6] \tag{11}$$

From the optical investigation of the very acidic solutions data for the first two of these protonation constants have been obtained: $pK_1 = 2.5$, $pK_2 = 2.1$ (section 3). These data, however, are uncertain because of the doubts expressed in section 3 as to whether the color changes presented in Figure 2 are due to the simple deprotonation of $Ti_2O_5 \cdot aq^{2+}$ (reaction 3). We consider it more likely that the complex existing below pH 1 is mononuclear which however has no influence on function 11 at pH values >3.

Equation 11 is obtained by starting from

$$\bar{x} = \sum_{x=1}^{6} x[Ti_2O_5(OH)_x] \Bigg/ \sum_{x=0}^{6} [Ti_2O_5(OH)_x]$$

and substituting the concentrations of the complexes $Ti_2O_5(OH)_x^{(2-x)+}$ from (10).

According to the curve of Figure 3, the uncharged yellow complex ($Ti_2O_5(OH)_2$) of solutions of pH 3 contains at least four water molecules coordinated to the two metal atoms: $(H_2O)_2Ti(OH)O_5Ti(OH)(OH_2)_2^{2+}$. There might, however, be more than four. The fact that the experimental points in Figure 3 do not follow the rise of the calculated curve after $\bar{x} = 5.5$ might indicate further deprotonation, yet it can also be explained by the formation of new species containing more than one peroxo group per titanium. The occurrence of such complexes in alkaline solutions containing an excess of H_2O_2 has been proved.[8,11,12]

5. Peroxotitanium Chelates.—The formula $(H_2O)_y\text{-}TiO_5Ti(OH_2)_y^{2+}$ from which the series of complexes $Ti_2O_5(OH)_x^{(2-x)+}$ can be derived by detaching protons suggests the feasibility of a replacement of the coordinated water by the ligand atoms of chelating agents. Peroxotitanium oxalates were indeed described as early as 1907[21] and again about half a century later.[6] However, these amorphous solids have never been well characterized. Sweetser and Bricker[22] observed a color change when ethylenediaminetetraacetic acid was added to the acidic orange solutions of peroxotitanium. The adduct contains Ti, H_2O_2, and EDTA in the ratio of 1:1:1[23] and its formation is the basis of a complexometric titration procedure for the determination of Ti.[24]

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[21] A. Mazzucchelli, *Gazz. Chim. Ital.*, **37** (II), 545 (1907); **40** (I), 666 (1910).

[22] P. B. Sweetser and C. E. Bricker, *Anal. Chem.*, **26**, 195 (1954).

[23] S. Musha and K. Ogawa, *Nippon Kagaku Zasshi*, **78**, 1686 (1957).

[24] G. Schwarzenbach and H. Flaschka, "Complexometric Titrations," Methuen, London, 1969, p 200.

Since the number of water molecules coordinated to each metal atom in the complex $Ti_2O_5^{2+}$ is at least $y = 3$ (section 4), terdentate ligands should be especially well suited to chelate peroxotitanium. They should be oxygen donors mainly because of the pronounced A character of d^0 Ti(IV).

5.1. The Job diagrams (Figures 4–6) demonstrate the formation of complexes with the terdentate anions of diglycollic acid $O(-CH_2-COOH)_2$ ($=H_2Digl$), iminodiacetic acid $HN(-CH_2-COOH)_2$ ($=H_2Im$), and α,α'-dipicolinic acid ($=H_2Dipic$). The optical density D_1 of mixtures of peroxotitanium and ligand is plotted *vs.* the ratio $x = [Ti]_t/c$, c being the sum of the total concentrations of titanium and ligand ($[Ti]_t + [L]_t = c$), which was kept constant in all the mixtures which all were of pH 3.

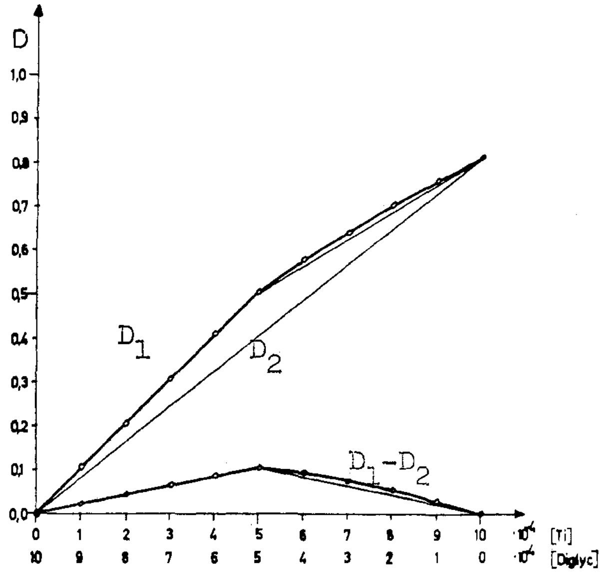

Figure 4.—Continuous-variation curves of peroxotitanium with diglycollic acid, λ 363 nm. The acidity was kept constant at pH 3; peroxotitanium concentration, $[Ti]_t = 0 \rightarrow 10 \times 10^{-4}$ *M;* ligand concentration, $[chel]_t = 10 \times 10^{-4} \rightarrow 0$ *M*.

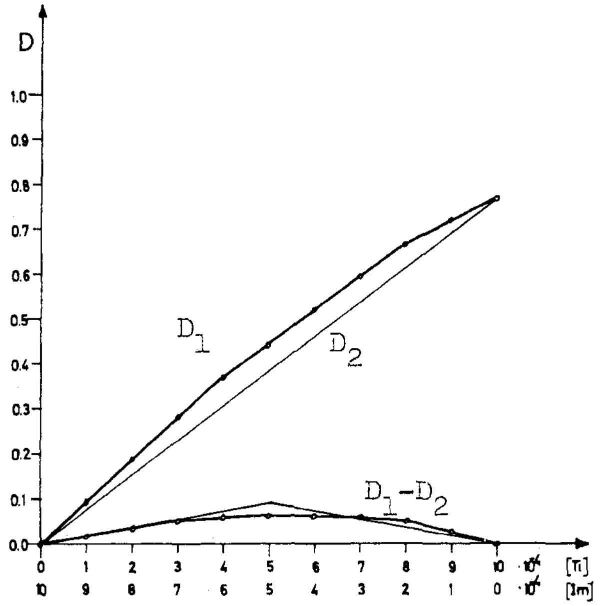

Figure 5.—Continuous-variation curves of peroxotitanium with iminodiacetic acid, λ 370 nm. The acidity was kept constant at pH 3; peroxotitanium concentration, $[Ti]_t = 0 \rightarrow 10 \times 10^{-4}$ *M;* ligand concentration, $[chel]_t = 10 \times 10^{-4} \rightarrow 0$ *M*.

If no reaction would take place between peroxotitanium and the chelating agent, a linear rise of the optical density with x would be observed, that is, the straight line D_2. The difference ($D_1 - D_2$) shows a pronounced maximum at $x = 0.5$ in at least two of the three figures which proves unequivocally the formation of a complex containing Ti and L in the ratio of 1:1. The molar extinction coefficients of unchelated and chelated peroxotitanium are similar and the difference ($D_1 - D_2$) therefore is only a comparatively small quantity. It is quite clear, however, and noteworthy that it rises linearly to the maximum but does not fall off as a straight line for the solutions containing an excess of peroxotitanium ($x > 0.5$). This is easily explained by the formation of a 2:2 complex $(chel)TiO_5Ti(chel)^{2-}$ and a 2:1 adduct $(chel)TiO_5Ti(OH_2)_y$, providing a further indication that the peroxotitanium complexes are dinuclear. Not only does the deprotonation from $n = 3$ to 4 proceed in two steps (section 3) and that from $n = 4$ to 6 in four steps (section 4) but also the chelation to an adduct containing Ti and L in the ratio of 1:1 proceeds stepwise. This is also demonstrated by the absence of isosbestic points in Figure 7, showing the absorption spectra of solutions of the same $[Ti]_t$ containing varying amounts of dipicolinic acid.

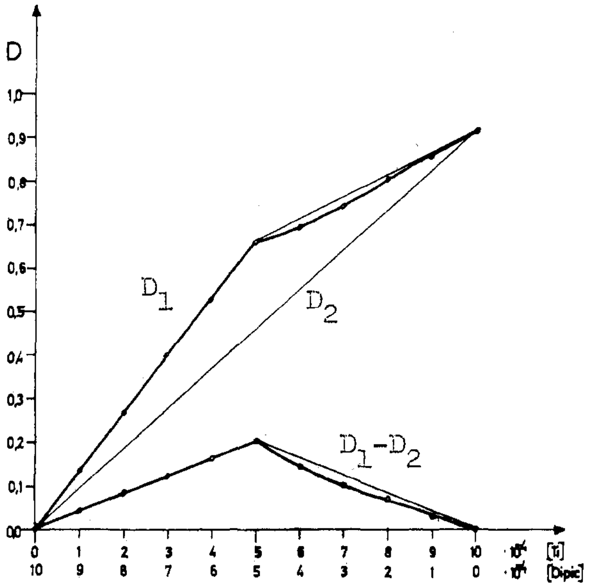

Figure 6.—Continuous-variation curves of peroxotitanium with dipicolinic acid, λ 355 nm. The acidity was kept constant at pH 3; peroxotitanium concentration, $[Ti]_t = 0 \rightarrow 10 \times 10^{-4}$ *M;* ligand concentration, $[chel]_t = 10 \times 10^{-4} \rightarrow 0$ *M*.

5.2 The formation of peroxotitanium complexes with the three terdentate chelating agents follows also from neutralization curves taken on mixtures made up from the standard solution A (diluted to

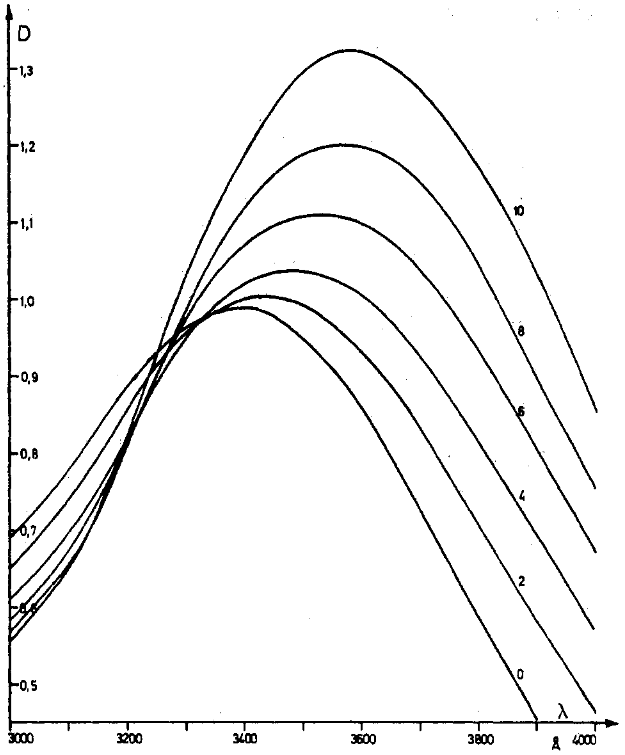

Figure 7.—Spectra of peroxotitanium of $[Ti]_t = 10^{-3}$ *M* and $[H_2O_2] = 10^{-2}$ *M* containing increasing amounts of dipicolinic acid from 0 to 10×10^{-4} *M*.

$[Ti]_t = 5 \times 10^{-3}$ *M*) and containing 1 molecule of the protonated ligand H_2chel per titanium. Only the result with dipicolinic acid is presented in Figure 8, where "*a*" again denotes the moles of NaOH added per Ti. Curve 1, which was observed, should be compared with the curve obtained without the chelating agent (Figure 1) and the one obtained with H_2Dipic alone (curve 2, Figure 8, which is displaced 5 *a* units to the right). The pronounced pH jump at $a = 5$ of curve 1 suggests that a single species is present in the pH range 4–5. Four of the five OH^- used per Ti are neutralized in the formation of $Ti_2O_5(OH)_2$ and the fifth H^+ is formed in the chelation process

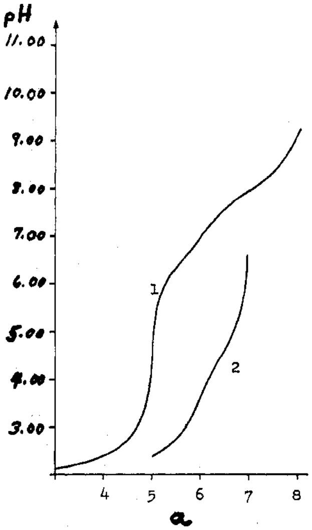

Figure 8.—Alkalimetric titration of standard solution A diluted to $[Ti]_t = 5 \times 10^{-3}$ *M*, $[H_2O_2] = 5 \times 10^{-2}$ *M*, and $\mu = 0.1$ ($NaClO_4$) with 1 mol of dipicolinic acid per Ti (curve 2 is obtained when H_2Dipic is titrated without peroxotitanium.

$$Ti_2O_5(OH)_2 + 2H_2Dipic \longrightarrow Ti_2O_5(Dipic)_2^{2-} + 2H^+ + 2H_2O \quad (12)$$

Above pH 6 more OH^- is neutralized, possibly due to process 13, causing a clearly visible inflection at $a = 6$.

$$Ti_2O_5(Dipic)_2^{2-} + 2OH^- \longrightarrow Ti_2O_5(OH)_2(Dipic)_2^{4-} \quad (13)$$

Above pH 8 the chelate is apparently decomposed according to

$$Ti_2O_5(OH)_2(Dipic)_2^{4-} + (x - 2)OH^- \longrightarrow Ti_2O_5(OH)_x^{(x-2)-} + 2Dipic^{2-} \quad (14)$$

As is always the case with solutions containing the dinuclear anionic species $Ti_2O_5(OH)_x^{(x-2)-}$, condensation processes (section 4) prevent accurate equilibria studies. Curve 1 of Figure 8 was obtained by titrating rapidly with an automatic titrator. The curve does not represent final equilibria data and is unsuitable for mathematical analysis.

The neutralization curves obtained with peroxotitanium and diglycollic acid as well as with iminodiacetic acid (which correspond to curve 1 in Figure 8) show definitely that the chelates $Ti_2O_5(Digl)_2^{2-}$ and $Ti_2O_5(Im)_2^{2-}$ are much less stable than the dipocolinate complex. For the iminodiacetate, this follows clearly also from the optical investigation (Figure 5, no sharp break at $x = 0.5$). Dipicolinic acid is superior to iminodiacetic acid for the complexation also of many other cations,[25] especially metal cations of A character,[26] when the process is taking place at low pH values where the metal ion has to compete with the hydrogen ion for the chelating anion. The special stability of the peroxotitanium dipicolinate is therefore not surprising.

5.3 From curve 1 in Figure 8 it can be deduced that the 1:1 mixture of titanium and dipicolinic acid in the presence of an excess of H_2O_2 contains at pH 4–5 a definite complex species $Ti_2O_5(Dipic)_2^{2-}$. An attempt was made to isolate this complex in the form of a salt which met with immediate success. One mole of dipicolinic acid per mole of Ti was added to standard solution A; the mixture was neutralized to pH 4.5 (which needs 5 mol of alkali metal hydroxide per Ti) and concentrated under vacuum. Well-developed orange-yellow crystals of the following salts were obtained: $K_2[Ti_2O_5(Dipic)_2] \cdot 5H_2O$ and $Na_2[Ti_2O_5(Dipic)_2] \cdot 8H_2O$.

The water present in these salts is given off stepwise. In the potassium salt, one H_2O is lost very easily, two are bound considerably more firmly, and the last two H_2O's cannot be removed without producing O_2 as well. The eight water molecules of the sodium salt are given off at different temperatures in two groups of four H_2O each. That the solution of the sodium salt contains a dinuclear anion has been demonstrated by ebullioscopic measurements, using a saturated NaCl solution as solvent.[27]

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(25) G. Anderegg and E. Bottari, *Helv. Chim. Acta*, **48**, 887 (1965).
(26) I. Grenthe, *Acta Chem. Scand.*, **17**, 2487 (1963); **18**, 293 (1964).
(27) B. Magyar, *Helv. Chim. Acta*, **48**, 1259 (1965); **51**, 194 (1968).

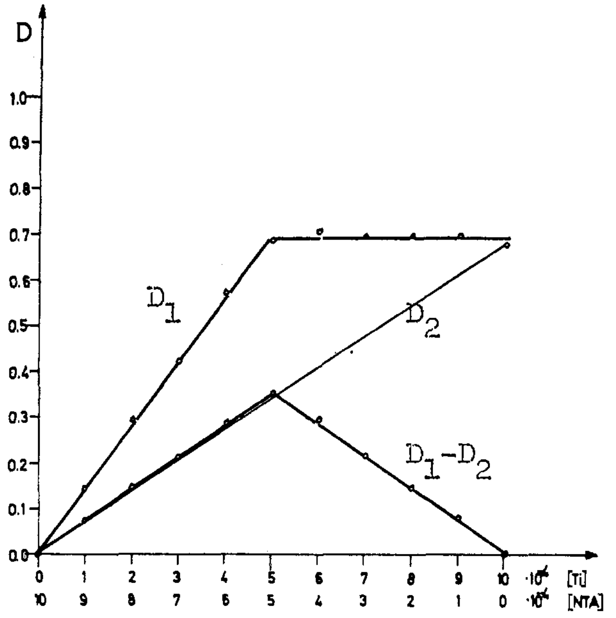

Figure 9.—Continuous-variation curves of peroxotitanium with nitrilotriacetic acid, λ 375 nm. The acidity was kept constant at pH 3; peroxotitanium concentration, $[Ti]_t = 0 \rightarrow 10 \times 10^{-4}\ M$; ligand concentration, $[chel]_t = 10 \times 10^{-4} \rightarrow 0\ M$.

An alkali metal free complex of peroxotitanium and dipicolinic acid has also been obtained, which seems to be mononuclear. It forms orange-red rhombohedra of the composition $[TiO_2(Dipic)]\cdot 4H_2O$ and behaves as a very strong acid.

5.4 It was to be expected that peroxotitanium would also form a chelate with the quadridentate anion (NTA^{3-}) of nitrilotriacetic acid. The curves obtained in applying the continuous variation method are shown in Figure 9 and demonstrate again the formation of a complex containing one molecule of the ligand per titanium. The color change during complexation is more pronounced with NTA than with terdentate ligands and the difference in optical density is quite appreciable at λ 375 nm. Furthermore $(D_1 - D_2)$ rises linearly up to $x = 0.5$ and decreases as a straight line afterward in contrast to the curves of Figures 4–6. From both observations we can guess that the NTA chelate might be mononuclear.

In the alkalimetric titration of solution A, to which 1 mol of the dialkali metal salt of nitrilotriacetic acid has been added, the pH jumps sharply between 4.5 and 9 (Figure 10) after the addition of 4 mol of OH^- per metal. A complex with the charge 2− per Ti must be the only species present in this pH range, and when we assume it to be mononuclear, its formation has to be formulated with

$$Ti(O_2)OH^+ + HNTA^{2-} \longrightarrow Ti(O_2)(NTA)OH^{2-} + H^+ \quad (15)$$

This complex could also be isolated in the form of a well-crystallized lemon yellow salt: $K_2[Ti(O_2)(NTA)OH]\cdot 3H_2O$. All the three water molecules are lost simultaneously and long before O_2 is given off and it seems that they are not coordinated to the metal.

5.5 The formation of the EDTA complex of peroxotitanium in solution has been mentioned 15 years ago.[22] It contains Ti, O_2, and the chelating agent in the ratio

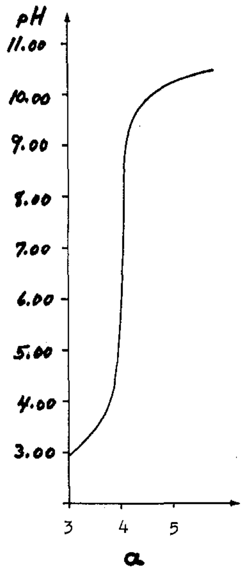

Figure 10.—Alkalimetric titration of standard solution A diluted to $[Ti]_t = 5 \times 10^{-3}\ M$, $[H_2O_2] = 5 \times 10^{-2}\ M$, and $\mu = 0.1$ ($NaClO_4$) with 1 mol of the disodium salt of nitrilotriacetic acid per Ti.

1:1:1.[23] However, the charge of the complex species is not positively known. We again started from solution A, obtained from $TiCl_4$, and added 1 mol of the dialkali metal salt of ethylenediaminetetraacetic acid. The alkalimetric titration curve shows a sharp jump from pH 6 to 8 after the addition of 4 mol of strong base (the same amount needed to produce $Ti_2O_5(OH)_2$) which leads to the formulation

$$TiO_2(OH)^+ + H_2EDTA^{2-} \longrightarrow 2Ti(O_2)EDTA^{2-} + H^+ \quad (16)$$

From the neutralized solution the solid complex potassium salt was obtained, which forms orange monoclinic prisms of the composition $K_2[Ti(O_2)EDTA]\cdot H_2O$. All our preparations were somewhat deficient in potassium. The molecule of H_2O is easily removed and does not seem to be coordinated.

5.6. The infrared spectra of the crystallized complexes are given in Figures 11–14 for the frequency range 650–1100 cm⁻¹. According to Griffith[28] the vibrational modes of the peroxide grouping of the peroxo complexes of various metals fall between 800 and 1000 cm⁻¹ and also our new peroxotitanium compounds show strong bands in this region. For those which we consider to be metal peroxide group bands the frequency is given in the figures.

6. **Conclusions.**—Our experiments show definitely that peroxotitanium is present in very acidic solutions as a cation with a single charge per metal. The complex is probably mononuclear TiO_2OH^+ below pH 1, but condenses to a dinuclear species at least between pH 1 and 3, and the unit Ti_2O_5 appears to be especially stable. The first products obtained on alkalization are the deprotonation products of $Ti_2O_5\cdot aq^{2+}$ of the general formula $Ti_2O_5(OH)_x^{(2-x)+}$. These species condense slowly to the insoluble peroxotitanium hydrate $TiO_3(H_2O)_x$, x being between 1 and 2. The dinuclear unit is present also in the peroxotitanium chelates formed with

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[28] W. P. Griffith, *J. Chem. Soc.*, 5248 (1964).

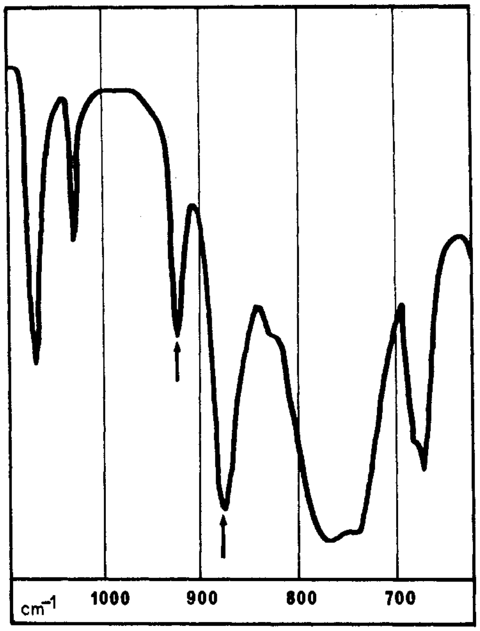


Figure 11.—Infrared spectrum of $K_2[Ti_2O_5(Dipic)_2] \cdot 5H_2O$ where the arrows indicate peroxide band frequencies at 927 and 879 cm^{-1}.

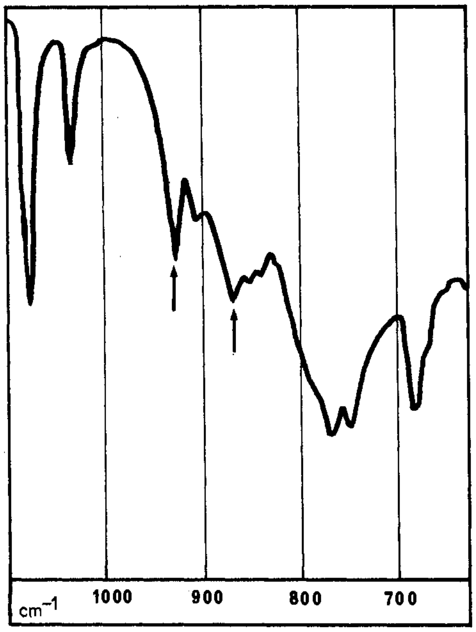
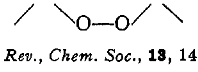


Figure 12.—Infrared spectrum of $TiO_2(Dipic) \cdot 4H_2O$ where the arrows indicate peroxide band frequencies at 929 and 869 cm^{-1}.

terdentate ligands $Ti_2O_5(chel)_2{}^{2-}$. The quadridentate nitrilotriacetate and the sexadentate anion of EDTA form mononuclear complexes however.

Condensation products which are only dinuclear are seldom encountered in the hydrolysis of metal–aquo ions.[29] We believed that the special stability of the Ti_2O_5 unit might be due to the following structure with two five-membered chelate rings which are so preferentially formed in the chemistry of chelates. From models we deduced that such an arrangement should be practically free of strain.



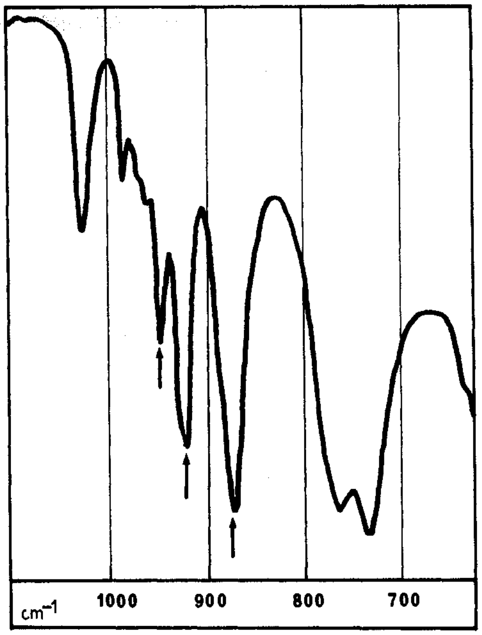


Figure 13.—Infrared spectrum of $K_2[TiO_2[OH)NTA] \cdot 3H_2O$ where the arrows indicate peroxide band frequencies at 948, 923, and 872 cm^{-1}.

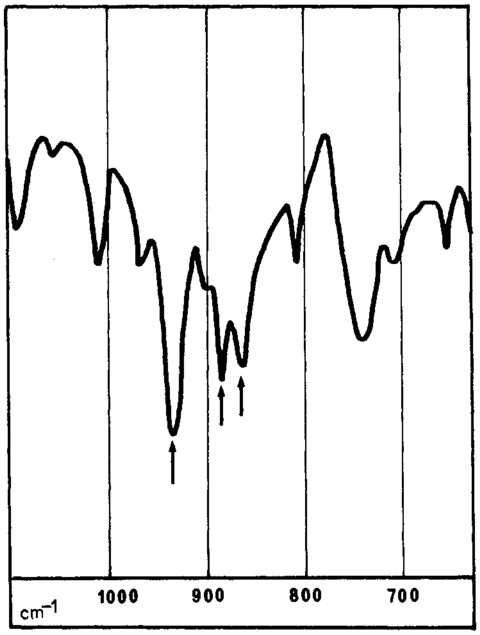


Figure 14.—Infrared spectrum of $K_2[TiO]_2EDTA)] \cdot H_2O$ where the arrows indicate peroxide band frequencies at 935, 883, and 863 cm^{-1}.

The crystal structure of potassium peroxotitanium dipicolinate[30] revealed, however, that the two metal atoms are bonded by a single μ-oxygen bridge and that the peroxo group apparently occupies only one coordination site. Such a structure explains of course the ease by which the dinuclear complexes break up in mononuclear species by raising the acidity or by adding nitrilotriacetate or EDTA.

The conspicuous color of the peroxotitanium complexes certainly is due to an electron transfer from the ligand $O_2{}^{2-}$ to the metal cation. The more basic the

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(29) L. G. Sillén, *Quart. Rev., Chem. Soc.*, **13**, 148 (1959).

(30) D. Schwarzenbach, *Inorg. Chem.*, **9**, 2391 (1970).

TABLE I

		Analyses, %											
	Formula	K or Na		Ti		O_2 (peroxide)		C		H		N	
Compound	weight	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$K_2[Ti_2O_5(Dipic)_2]\cdot 5H_2O$ $K_2Ti_2O_{18}C_{14}H_{16}N_2$	678.17	11.55	11.1	14.70	14.5	9.43	9.5	24.75	24.70	2.07	2.13	4.13	4.39
$Na_2[Ti_2O_5(Dipic)_2]\cdot 8H_2O$ $Na_2Ti_2O_{21}C_{14}H_{22}N_2$	700.00	6.56	6.7	14.26	14.2	9.13	9.2	24.00	24.00	3.17	2.88	4.00	4.23
$[Ti(O_2)(Dipic)]\cdot 4H_2O$ $TiO_{10}C_7H_{11}N$	319.01	0.00	0.0	15.63	...	10.3	10.2	26.35	26.42	3.47	3.22	4.39	4.58
$K_2[Ti(O_2)OH(NTA)]\cdot 3H_2O$ $K_2TiO_{12}C_6H_{13}N$	419.23	18.66	18.6	11.90	12.0	7.64	7.4	17.18	17.37	3.13	2.65	3.34	3.58
$K_2[Ti(O_2)(EDTA)]\cdot H_2O$ $K_2TiO_{11}C_{10}H_{14}N_2$	466.25	16.78	14.3	10.72	11.0	6.87	6.8	25.75	26.5	3.03	3.3	6.00	6.3

further ligands (in the series OH_2, $-COO^-$, $\geqslant N$, OH^-) the more difficult it becomes to reduce Ti(IV) to Ti(III) and the higher apparently is the frequency of the intense absorption band.

Experimental Part

1. **Stock Solution.**—A 37.94-g (0.2-mol) amount of freshly distilled $TiCl_4$ was added drop by drop to 150 ml of hydrogen peroxide (free of any stabilizer) containing 2.3 mol of H_2O_2 which was kept at about −30°. The addition took from 2 to 3 hr and vigorous stirring was essential. The temperature should not rise above −25° in order to prevent evolution of O_2 but should not be too low either to prevent $TiCl_4$ from solidifying. Solid $TiCl_4$ reacted very slowly and accumulated in the suspension which, when later warmed up, sometimes caused an almost explosive decomposition (danger!). After the addition of $TiCl_4$, the homogeneous deeply red mixture was diluted to 500 ml with ice water. This stock solution with $[Ti]_t = 0.4\ M$, $[Cl^-] = 1.6\ M$, and $[H_2O_2] = 4\ M$ was kept at −10° and did not show any signs of change after many months.

2. **Solutions for the Potentiometric and Optical Studies.**—The standard solution A was prepared by diluting the stock solution four times and kept unchanged at 2° for about 2 weeks. The solutions B for the spectrophotometric investigation between pH 1 and 3 (section 3) were obtained by adding to 10 ml of solution A the necessary quantities of KCl and HCl (or NaOH) and diluting to 1000 ml. For taking the curve presented in Figure 1, 10 ml of 1 M $NaClO_4$ was added to 5 ml of standard solution A, the mixture was diluted to 100 ml, and the titration was started immediately.

For taking the Job curves (Figures 4, 5, 6, 9) a solution of peroxotitanium of $[Ti]_t = 10^{-3}\ M$ and solutions of the chelating agents of $[chel]_t = 10^{-3}\ M$ had to be prepared, both of ionic strength $\mu = 0.1$. These solutions had to be mixed in the ratios 1:9 to 9:1 to solutions of approximately pH 3. To 10 ml of standard solution A, 100 ml of 1 M KCl was added as well as 30 ml of 0.1 M NaOH and diluted to 1000 ml. On the other hand, diglycollic acid or iminodiacetic acid, dipicolinic acid, and the monoalkali metal salt of nitrilotriacetic acid, respectively, were made up with KCl to $10^{-3}\ M$ solutions without adding any strong base. The preparation of the titanium solution and mixing with the chelating agent took about 3 min and the optical density was then determined without delay.

3. **$K_2[Ti_2O_5(Dipic)_2]\cdot 5H_2O$.**—The solution of 1.67 g of dipicolinic acid (=0.01 mol) was added to 100 ml of standard solution A; the mixture was neutralized to pH 4.5 with 500 ml of 0.1 M KOH and concentrated under vacuum between 20 and 25° to a volume of about 50 ml. A slight turbidity which may appear can be removed by adding some more base. The solution was now placed in a desiccator over anhydrous $CaCl_2$. The orange-yellow monoclinic plates formed within a few days were washed with very little cold water and dried over 80% H_2SO_4. If the drying was done below 30% relative humidity, the crystals got turbid and lost water. The thermograms taken in dry N_2 of 1 atm reveal the loss of 1 H_2O at 50° and 2 further H_2O at 75°. The last 2 H_2O come off at 150–175° together with O_2 from the peroxo group. Under vacuum (0.01 Torr) elementary oxygen starts to be given off at 100°.

4. **$Na_2[Ti_2O_5(Dipic)_2]\cdot 8H_2O$.**—The orthorhombic orange-yellow prisms of the sodium salt were obtained with the same procedure after neutralizing with NaOH instead of KOH. Below 20% relative humidity, the crystals lost water. The thermogram taken in dry N_2 of 1 atm reveals the loss of 4 H_2O at 75°, again of 4 H_2O at 125°, and of O_2 at 150°. Under vacuum 25% of the peroxo oxygen was given off at 50–60° and the remaining O_2 above 100°.

5. **$[Ti(O_2)(Dipic)]\cdot 4H_2O$.**—One mole of dipicolinic acid per Ti was added to solution A and the acidity of the homogeneous mixture was reduced by adding 4 mol of NaOH. The still strongly acidic orange solution was concentrated below 25° and then placed over 80% H_2SO_4. Orange-red triclinic prisms were formed within some days. When these were dissolved in water, a yellow-orange strongly acidic solution was obtained. Two H_2O were lost below 10% relative humidity. The thermogram taken in dry N_2 of 1 atm reveals the loss of 2 H_2O at 75°; the remaining water is given off together with O_2 at 150°.

6. **$K_2[Ti(O_2)OH(NTA)]\cdot 3H_2O$.**—The solution of 1.91 g of nitrilotriacetic acid (=0.01 mol) was added to 100 ml of standard solution A and the mixture was neutralized with 600 ml of 0.1 M KOH up to pH ∼6. The volume was now reduced considerably at a temperature not exceeding 25° and the salts were precipitated with ethanol. The separation of the very soluble peroxo complex from KCl was achieved by fractional crystallization, using water and ethanol containing some H_2O_2 as solvents. The lemon yellow crystals formed triclinic prisms which were kept over 80% H_2SO_4. Below 5% relative humidity all the three molecules of water were lost. Heated in dry N_2 ($p = 1$) the $3H_2O$ were given up at 80–100°, but there was no evolution of O_2 up to 180°.

7. **$K_2[TiO_2(EDTA)]\cdot H_2O$.**—The solution of 2.92 g of ethylenediaminetetraacetic acid (=0.01 mol) was added to 100 ml of standard solution A and the mixture was neutralized to pH ∼6 with 600 ml of 0.1 M KOH. The volume was now reduced considerably at a temperature not exceeding 25° and the salts were precipitated with ethanol. The separation of the very soluble peroxo complex from KCl was achieved by fractional crystallization, using water and ethanol containing some H_2O_2 as solvents. The orange-yellow crystals form monoclinic prisms and are kept over 80% H_2SO_4. All our preparations were somewhat deficient in potassium which probably is due to a partial protonation of a carboxylate group not coordinated. In an atmosphere below 5% relative humidity H_2O is slowly lost. Heated in dry N_2 ($p = 1$) one molecule of H_2O was given up at 90–110°, and there was no evolution of O_2 up to 170°.

8. **Analysis.**—The alkali metal content was determined by atomic absorption, Ti gravimetrically and C, H, and N by combustion (see Table I). In the peroxo dipicolinates the peroxide oxygen could be obtained by titration with $KMnO_4$. Nitrilotriacetic acid and ethylenediaminetetraacetic acid, however, are oxidized by permanganate, but a titration with Ce(IV) was possible.