

# STUDY OF THE FORMATION OF THE PEROXOTITANIUM(IV) COMPLEX

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A stopped-flow spectrophotometric method was used to study the formation of the peroxo-titanium(IV) complex in 0.1 N and 1 N perchloric, hydrochloric and sulphuric acid solutions. At both acid concentrations the highest rate was observed in the sulphuric acid solution. Increase of the acid concentration resulted in a slight increase in the rate.

Cryoscopy showed the peroxotitanium(IV) complex to be a monomer, while ion-exchange examinations indicated that it is a cation with a 1:1 composition. Its formation is a second-order process; in 0.1 N sulphuric acid solution at 25°, the rate constant is  $346 \text{ M}^{-1} \cdot \text{s}^{-1}$ . The logarithm of the stability constant of the complex is 3.80.

The complex of the titanium(IV) ion with hydrogen peroxide has long been used for the detection and determination of hydrogen peroxide. A number of publications have dealt with the stability and composition of the complex. It has been found that its composition is 1:1, but opinions are divided as to its structure. Since the absorption spectrum of the complex does not depend on the nature of the anion present, some authors have assumed cationic complexes with various compositions, e. g.  $[\text{TiO}_2(\text{H}_2\text{O})_3]^{2+}$  [1],  $[\text{Ti}(\text{H}_2\text{O}_2)]^{4+}$  [2],  $\text{Ti}(\text{OH})_2(\text{H}_2\text{O}_2)^{2+}$  [3] and  $[\text{TiO}_2(\text{OH})]^+$  [4]. In sulphuric acid medium SCHWARZ and GIESE [5] assumed an anionic complex of composition  $[\text{TiO}_2(\text{SO}_4)_2]^{2-}$ , but the studies by PATEL and MOHAN [6] did not confirm the formation of such a compound. From the virtual immobility of the complex in an electric field, the latter authors assumed a neutral species,  $\text{TiO}_2\text{SO}_4 \cdot 2 \text{H}_2\text{O}$ . The results of investigations into the stability of the complex have been reviewed by VASIL'EV and VOROB'EV [7], who also made a detailed examination of the effects of the nature and concentration of the acid used on the stability of the complex. It was found that in the case of perchloric acid  $\log K$  increases linearly with the ionic strength, while for sulphuric, hydrochloric and nitric acids saturation curves were obtained; no reason was given for this. The thermodynamic stability constant of the complex was calculated:  $\log K=3.7$ .

In spite of the extensive investigations, we know of no work in which the kinetics of formation of the peroxo complex have been studied, whereas in our view such a study might well provide information of use in understanding this complex. In the present paper we report results obtained in a kinetic study of the complex-formation reaction.

### Experimental

**Titanium(IV) stock solutions:** An equal volume of distilled water was added to titanium(IV) chloride drop by drop and the hydrogen chloride evolved was pumped off. Following this, the calculated amount of concentrated perchloric, hydrochloric or sulphuric acid was added, and air was then passed through the fairly viscous liquid for several hours. With ice-cooling and effective stirring, the solution was next diluted to the desired concentration with distilled water. The acid concentrations of the solutions were determined by pH-metric titration, and the titanium(IV) contents gravimetrically.

**Hydrogen peroxide solution:** This was prepared by diluting MERCK Perhydrol with acid of appropriate nature and concentration.

**Peroxititanium(IV) solution:** 12 g (100 mmole) sodium hydrogen sulphate and 12.0 ml 30% hydrogen peroxide (ca. 100 mmole) were added to 12 g (50 mmole) titanium(IV) sulphate, and the volume was made up to 50 ml with distilled water. After several hours' intensive stirring, the bulk of the solid material had dissolved up to give a deep-red peroxotitanium(IV) sulphate solution. The hydrogen peroxide content of the solution was determined by permanganometric titration, the titanium(IV) content gravimetrically, and the hydrogen ion and hydrogen sulphate concentration by pH-metric titration. Peroxititanium(IV) perchlorate was obtained using barium perchlorate in excess to precipitate the sulphate in an aliquot of the former solution, the precipitate being removed by centrifugation. The hydrogen peroxide, titanium(IV) and hydrogen ion concentrations of the resulting solution were measured as previously, while the perchlorate content was determined indirectly: complete cation-exchange was carried out on DOWEX—50 cation-exchange resin in the R—H form, and the acid obtained was titrated. The perchlorate concentration was taken as equal to the hydrogen ion concentration thus measured.

**Kinetic measurements:** A laboratory-constructed stopped-flow apparatus consisting entirely of teflon was used. Solutions adjusted to 25° were mixed, and complex formation was followed via measurement of the transmittance of the complex at 410 nm. The transmittance *vs.* time curves were recorded on an RFT OG2—21 memory oscilloscope, and enlarged photographs of these were evaluated. In the event of minor changes in transmittance, the scale was expanded electrically.

**Ionic weight determination:** In order to determine the degree of aggregation of the species in solution, cryoscopic measurements were carried out in a Glauber salt melt [8]. The following correlation was used to evaluate the cryoscopic measurements:

$$PN = \frac{K}{K_0} = \frac{g_a \Delta T}{3.40 n_b}$$

where  $PN$  is the particle number,  $g_a$  is the amount of solvent (here Glauber salt) in g,  $\Delta T$  is the measured freezing-point depression in °C,  $K_0$  is the molecular freezing-point depression, and  $n_b$  is the number of moles of solute. About 2 mmole peroxotitanium(IV) was added to 13 g anhydrous sodium sulphate in the cryoscope tube, together with sufficient water for the total amount of water to be 20 g. The freezing-point depression was measured with a Beckmann thermometer. After determination of the depression, the mixture was remelted and samples were

taken from it for determination of the peroxide, titanium(IV) and hydrogen ion concentrations.

*Ion-exchange examinations:* 3 g of DOWEX—2 anion-exchange resin in the form  $R-SO_4$ , or 3 g of DOWEX—50 cation-exchange resin in the form  $R-H$ , was packed onto a glass-wool plug in a 9 mm diameter glass tube, 0.05 M sulphuric acid was sucked upwards from the bottom to remove all bubbles from the column, and the acid was then let down to the level of the resin. A solution to be examined, similarly 0.05 M in sulphuric acid, was transferred to the column at a low rate (1 drop per 2—3 sec). Then the column was washed with 30 ml 0.05 M sulphuric acid. The solution dripping through during exchange and washing was collected in a 50 ml volumetric flask, and the volume was made up to the mark with 0.05 M sulphuric acid. The absorbance of the solution was measured at 410 nm.

### Experimental results

Fig. 1 presents some typical peroxo complex-formation curves. It can be seen that for an acid concentration of 0.1 N, the complex is formed at the same rate in perchloric and hydrochloric acids; in sulphuric acid the reaction is substantially faster, and accordingly, equilibrium is established in a shorter time. If the acid concentration is increased by a factor of ten in the cases of perchloric and hydro-

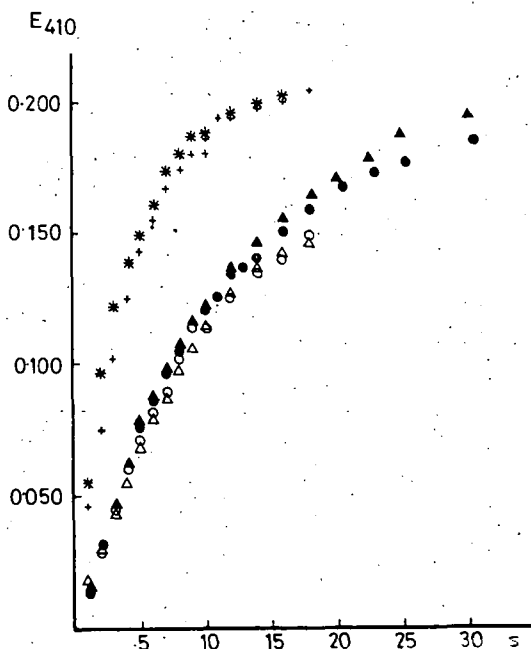


Fig. 1. Formation of the peroxotitanium(IV) complex in acids of different concentrations. + 0.1 N  $H_2SO_4$ ; \* 1 N  $H_2SO_4$ ; O 0.1 N  $HClO_4$ ; ● 1 N  $HClO_4$ ; Δ 0.1 N HCl; ▲ 1 N HCl.

chloric acids, only a slight rate change is observed in the initial stage of the reaction; in the higher conversion range, however, the curves are situated higher than those recorded at the lower acid concentration. A slight rate increase can be observed in the case of sulphuric acid.

In sulphuric acid medium the concentration of either the titanium(IV) or the hydrogen peroxide was maintained constant, and a study was made of the dependence of the reaction rate on the concentration of the other reaction partner. When the logarithm of the initial rate was plotted as a function of the logarithm of the concentration of the partner, in both cases a straight line with unit slope was obtained. On the increase of the titanium(IV) or hydrogen peroxide concentration by one order of magnitude, the overall order of the reaction decreased from 2 to 1. All these facts show that the reaction is a first-order one with respect to both titanium(IV) or hydrogen peroxide.

Examinations as to the composition of the complex gave a composition of 1:1, in agreement with the literature.

In the knowledge of the molar absorptivity of the complex, and of the limiting absorbance ( $E_\infty$ ) measured at the end of the reaction, as well as the analytical concentrations of titanium(IV) and hydrogen peroxide ( $[Ti]_T$ ,  $[H_2O_2]_T$ ), the stability constant was determined from

$$K = \frac{E_\infty/\epsilon}{([Ti]_T - E_\infty/\epsilon)([H_2O_2]_T - E_\infty/\epsilon)}$$

(see Table I).

In sulphate medium, values of 0.98 and 1.00 were obtained for the particle number cryoscopically. With this method, peroxotitanium(IV) perchlorate similarly proved to be a monomer ( $PN=0.92$ ). However, this does not establish the state of

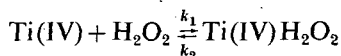
Table I  
Stability constant of the peroxotitanium(IV)  
complex in 0.1 N sulphuric acid

$(H_2O_2)_T \times 10^{-4} \text{ M}$	$(Ti)_T \times 10^{-4} \text{ M}$	$E_\infty$	$\log K$
2	2	0.055	3.63
2	4	0.100	3.99
2	8	0.110	3.75
2	10	0.110	3.64
2	20	0.132	3.93
2	2	0.060	3.82
4	2	0.097	3.93
6	2	0.108	3.88
8	2	0.108	3.71
10	2	0.110	3.64
20	2	0.131	3.89
			mean: 3.80

aggregation of the peroxotitanium(IV) perchlorate, for the large sulphate excess could have led to the disaggregation of possible polymeric ions.

### Discussion

The kinetic information obtained indicates that complex formation between titanium(IV) ions and hydrogen peroxide in sulphuric acid medium is a second-order reaction with 1:1 stoichiometry. The stability of the complex formed is not too high, and therefore the back-reaction too must be taken into consideration in the kinetic evaluation.



for which

$$\frac{dx}{dt} = k_1(a_0 - x)(b_0 - x) - k_2x,$$

where  $x$  is the concentration of the formed complex at the given time, and  $a_0$  and  $b_0$  are the initial concentrations of titanium(IV) and hydrogen peroxide, respectively. The values of the constants  $k_1$  calculated from the integrated form of this equation are given in Table II. Our value of the stability constant was used in the calculation. The data demonstrate that the above simple kinetic picture describes the experimental results satisfactorily. If the thermodynamic stability constant given by VASIL'EV and VOROB'EV is used in the calculations,  $k_1$  is about 5% larger.

The finding that the reaction has a higher rate in sulphuric acid medium than in perchloric or hydrochloric acids shows that the titanium(IV) species in various solutions have different reactivities. In the presence of weakly-complexing acids an oxygen-bridged aquotitanium(IV) polyion  $[\text{TiO}(\text{H}_2\text{O})_4]_n$  may be assumed, whereas in sulphuric acid medium the polymer presumably contains sulphate  $[(\text{TiOSO}_4)_x(\text{H}_2\text{O})_y]_n$ , too. The ion-exchange investigations reveal that in 0.1 N

Table II

Rate constant for formation of the peroxotitanium(IV) complex in 0.1 N sulphuric acid

$\text{H}_2\text{O}_2$ M.10 <sup>4</sup>	Ti(IV) M.10 <sup>4</sup>	Conversion %	$k_1$ M <sup>-1</sup> s <sup>-1</sup>	$\text{H}_2\text{O}_2$ M.10 <sup>4</sup>	Ti(IV) M.10 <sup>4</sup>	Conversion %	$k_1$ M <sup>-1</sup> s <sup>-1</sup>
4	2	12.85	462.3	2	4	12.14	361.4
4	2	22.14	349.3	2	4	22.15	349.3
4	2	30.35	369.3	2	4	30.71	369.7
4	2	37.85	383.9	2	4	38.57	383.9
4	2	42.85	385.2	2	4	44.28	385.2
6	2	15.71	301.4	2	8	20.71	301.4
6	2	29.28	322.6	2	8	35.81	304.2
6	2	39.28	328.0	2	8	48.57	325.0
6	2	46.42	322.8	2	8	55.71	315.5
6	2	52.14	322.5	2	8	62.14	309.2
10	2	27.14	328.1	2	10	27.14	344.8
10	2	46.42	347.2	2	10	47.14	328.1
10	2	57.85	341.6	2	10	59.28	341.7
10	2	67.14	356.0	2	10	67.14	332.7
10	2	72.85	360.8	2	10	71.42	364.2

sulphuric acid about 80% of the titanium(IV) is present as a cationic complex, and about 20% as an anion. It is probable that the hydrogen peroxide attacks at the bridging O atoms and brings about disaggregation of the polyions. Since the ease of attack on the bridging O depends on the nature of the other ligands attached to the central titanium(IV) ion, it is understandable why the rate of formation of the peroxo complex will be different in the presence of different acids. If (disregarding aggregation of the titanium(IV)) a reaction of  $S_N2$  type were assumed, in the course of which hydrogen peroxide or  $\text{HO}_2^-$  (more nucleophilic than water) undergoes dissociative substitution, then the higher rate observed in sulphuric acid medium would be due to the substitution of the less nucleophilic sulphate ion occurring more rapidly than the exchange of water.

However, it would then be difficult to fit in our other findings with this picture. Let us consider the stock solutions with acid concentrations of 2.8 N, prepared as described earlier. When these were left to stand for several weeks, no precipitation was observed in the case of the sulphuric acid solution, whereas a large proportion of the titanium content was precipitated as an oxide hydrate from the solution prepared with perchloric and hydrochloric acids. This permits the conclusion that sulphate is the best stabilizer; the effect of chloride is much weaker, but it is perceptible on comparison with the low stability of the perchloric acid solution.

If an  $S_N1CB$  (conjugated base) mechanism were assumed, the peroxidation should lead to a more significant acid-dependence. The fairly low rate of the peroxidation reaction suggests an inner-sphere-type reaction.

Ion-exchange studies show that in 0.10 N sulphuric acid the peroxo-sulphato-titanium(IV) complex is present predominantly in cationic form, *ca.* 90% being bound to the cation-exchange resin, in comparison to only 10–15% for the anion-exchange resin in  $\text{R}-\text{SO}_4$  form. This finding is in agreement with the observations of earlier authors if it is taken into consideration that the results of the previous investigations (mentioned in the introduction) were obtained under different experimental conditions as regards the titanium(IV), hydrogen ion and sulphate concentrations.

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## ИЗУЧЕНИЕ ОБРАЗОВАНИЯ КОМПЛЕКСОВ ПЕРОКСОТИТАНА(IV)

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Методом "stopped-flow" — спектрофотометрии изучено образование комплексов пероксотитана(IV) в 0.1н и 1н растворах перхлорной-, соляной- и серной кислот. Наибольшие скорости образования наблюдались в растворах серной кислоты обеих концентраций. Увеличение концентрации кислоты приводило к небольшим возрастаниям скорости образования.

Образование комплекса пероксотитана(IV) состава 1:1, который по криоскопическим данным представляет собой мономер, а по ионообмену — катион, происходит по второму кинетическому порядку и в 0.1 н растворе серной кислоты константа скорости образования при 25 °C равна  $346 \text{ л} \cdot \text{моль}^{-1} \cdot \text{сек}^{-1}$ . Логарифм константы устойчивости комплекса равен 3.80