PEROXY TITANIUM OXALATE

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MAZZUCHELLI AND PONTANELLI¹ prepared a peroxy titanium oxalate complex of the formula Ti₃O₃(C₂O₄)₂ from a reddish oil, obtained by adding an excess of hydrogen peroxide, ethyl alcohol and ether to a solution of freshly precipitated titanic oxide in oxalic acid. Literature does not indicate any subsequent work on the peroxide titanium oxalate complexes. The complex, Ti₃O₃(C₂O₄)₂, could be considered as a derivative of the peroxide product, Ti₂O₅ which has been shown recently to be the decomposition product of the peroxide TiO₂ on storage.² In the present investigation, the method of preparation of the normal peroxide titanium oxalate and its properties are described.

When a solution of precipitated titanium hydroxide in excess of oxalic acid was treated with hydrogen peroxide, it was noticed that an orange red solution was obtained. The depth of the colour depended on the concentration of the hydrogen peroxide added. The absorption spectrum of the solution was different from that of the peroxide titanium sulphate solution investigated by Weissler.³ The solid could not be crystallized out from the solution but an amorphous red solid was, however, obtained by evaporation of the solution on a water-bath at 50°C. The solid, thus prepared, was found to have variable composition with respect to peroxo oxygen, even though excess of hydrogen peroxide was employed during the preparation. Exact conditions had, therefore, to be worked out for the preparation of a pure peroxide complex.

EXPERIMENTAL

Reagents Employed

1. Oxalic Acid (C.P.) was recrystallised thrice from distilled water and employed in the preparation of the complex.

2. Hydrogen Peroxide.—30% H₂O₂ (Merck) was used.

3. Pertitanic Acid.—The yellow pertitanic acid was precipitated by addition of dilute ammonia to an aqueous solution of purified titanium tetrachloride containing the calculated amount of hydrogen peroxide. The pertitanic acid, thus prepared, could be freed from chloride ions by repeated
washing with distilled water but ammonium ions could not be completely removed in this way. The precipitate was, therefore, initially washed with 0.001 N hydrochloric acid which facilitated the removal of ammonium ions. Final washing was effected with distilled water to remove the last traces of the chloride ions. Pertitaniic acid free from chloride and ammonium ions was employed for the preparation of the peroxy compounds of titanium. The purified pertitaniic acid, prepared from several samples of titanium tetrochloride, had the approximate composition TiO₅ (Table I).

Methods of Analysis

Estimation of Peroxy Oxygen.—Since the peroxy titanium oxalate complex was found to be slightly hygroscopic, precautions were taken to exclude moisture during weighing and transferring the complex. Peroxy oxygen in the complex was determined by the acidified potassium iodide method.⁴

Abel⁵ has pointed out that oxalic acid is oxidised to CO₂ by iodine. But experiments carried out in this laboratory on the mixtures of iodine and oxalic acid, both in the dark and in diffused daylight, indicated that there was no detectable oxidation of the oxalic acid by the aqueous iodine. Hence, it was inferred that oxalic acid did not interfere with the estimation of peroxy oxygen by the iodide method.

Estimation of Oxalate.—When the peroxy titanium complex was treated with dilute sulphuric acid, a mixture of hydrogen peroxide and oxalic acid was produced. The sum of the two was estimated by potassium permanganate titration. It is interesting to note in this connection that the estimation of oxalic acid could be carried out rapidly at the laboratory temperature (23°C) without heating the mixture. This is perhaps due to the catalytic effect of manganese sulphate which is produced during the hydrogen peroxide reduction by permanganate. Since the peroxy oxygen was estimated by the iodide method, the oxalate content could be computed.

Estimation of Titanium.—The peroxy titanium oxalate was ignited in a platinum crucible and the titanium dioxide produced was determined to compute the value of titanium.

Analysis by the Combustion Method.—Since the peroxy titanium oxalate complex contained inactive oxygen, the amount of water in the complex could not be obtained by difference. To determine water in the complex, combustion method was employed using about 50 mg. samples, when water and carbon dioxide produced during the combustion were absorbed by magnesium perchlorate and ascarite respectively. From the values of carbon
dioxide and water, the oxalate and water contents were computed. The titanium content of the complex was estimated by weighing the titanium dioxide residue in the boat. Since the per oxy oxygen, titanium, oxalate (C₂O₄⁻) and water in the complex were known, the inactive oxygen was calculated by difference. The results of analyses by the wet methods and the combustion method agreed well.

*Preparation of the Peroxy Titanium Oxalate Complex.*—About 30 g. of the slurry of pertitanic acid (Tᵢ = 2 g.) whose molar ratio of TiO₂:O (peroxy) was approximately 1·7:1, was mixed with large excess of oxalic acid (14 g.), when an orange red solution was obtained on shaking for about an hour. On concentrating the solution by passing dry air, most of the excess of oxalic acid was crystallized out. Concentration of the solution on water-bath had to be avoided to prevent the oxidation of oxalic acid by the per oxy oxygen. The mother liquor on further concentration yielded an orange red solid (peroxy titanium oxalate), containing some free oxalic acid, which was removed by repeated washing with alcohol. The sample was dried and analyzed. The experiment was repeated with different samples of pertitanic acid and the results are given in Table I, where experiments 1 to 3 show that the

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Molar composition of the pertitanic acid used (≈Ti₂O₅)</th>
<th>Molar composition of the red solution after addition of H₂O₂ + H₂C₂O₄</th>
<th>Average molar ratio of the various constituents in the solid complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>O*</td>
<td>Ti₂O₅</td>
<td>H₂O₂</td>
</tr>
<tr>
<td>1</td>
<td>1·67</td>
<td>1</td>
<td>1·00</td>
</tr>
<tr>
<td>2</td>
<td>1·70</td>
<td>1</td>
<td>1·00</td>
</tr>
<tr>
<td>3</td>
<td>1·63</td>
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<td>1·00</td>
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<td>4</td>
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<tr>
<td>9</td>
<td>1·65</td>
<td>1</td>
<td>1·98</td>
</tr>
<tr>
<td>10</td>
<td>1·70</td>
<td>1</td>
<td>1·00</td>
</tr>
</tbody>
</table>

* O = Peroxy oxygen obtained by KI Method.
complex has the average composition Ti$_2$O$_3$($C_2$O$_4$)$_2$, 7 H$_2$O. The lower peroxy content of the complex is obviously due to the lower peroxy oxygen content in the titanium peroxide employed as the starting material.

_Preparation of Pure Peroxy Titanium Oxalate Complex._—In this series of experiments, attempts were made to increase the amount of peroxy oxygen by addition of hydrogen peroxide in the starting solution, the rest of the procedure being the same as described above. The results are given in Table I, experiments 4 to 10.

The results of the last three experiments (8 to 10) show that in presence of large excess of hydrogen peroxide, the composition of the complex is TiO$_2$C$_2$O$_4$, 3·5 H$_2$O. On the other hand, when the amount of hydrogen peroxide added is low (experiments 4 to 7), the peroxy oxygen content in the final product obtained is less than the theoretical value of the complex TiO$_2$C$_2$O$_4$.

Tests for Ascertaining the Peroxide Linkage in the Complex._—Active oxygen in the peroxy complex may be present as perhydrate, where active oxygen is due to the hydrogen peroxide of crystallisation. Active oxygen may also be present as a peroxide forming a true peroxide linkage –O–O–. In order to find out the nature of the peroxy oxygen in the titanium oxalate complex, the following tests were carried out.

(1) _Ether Extract._—Ether extract$^6$ of the aqueous solution of the normal peroxy complex did not give any test for hydrogen peroxide, showing that the complex is not a perhydrate.

(2) _Vapours of the Complex Collected in Vacuum._—The peroxy complex was subjected to evacuation at room temperature for three hours and the vapours evolved from the complex condensed in a trap surrounded by liquid air. The aqueous condensate was free from any hydrogen peroxide, as tested by the titanium sulphate solution.

(3) _Krauss and Oettner Test$^4$ modified by Liebhafsky$^5._—Liebhafsky has stated that when potassium iodide reaction is carried out at a pH of 7·5–8·0, quantitative liberation of iodine would result only in the case of true peroxy compound, while oxygen is liberated when the compound contains hydrogen peroxide of crystallisation. When this test was applied to the peroxy titanium oxalate complex, it was noticed that iodine was liberated and not oxygen. It can, therefore, be concluded that the present complex is a true peroxy complex. Similar tests were given by the complexes containing lower peroxy oxygen content.
Effect of Storage on the Peroxy Complex.—It was observed that the complex faded in colour on storage, obviously due to the loss of peroxy oxygen. To study the rate of decomposition, the peroxy complex, $1.16 \text{Ti}:1.00 \text{(peroxy)}:1.15 \text{C}_2\text{O}_4:3.80 \text{H}_2\text{O}$, was kept in a weighing bottle in a desiccator free from moisture and the titanium and active oxygen contents were determined daily for about twelve days. The results of Fig. 1 show that there is a continuous loss of active oxygen from the complex. The analysis of the substance after twelve days showed that there was practically no loss of oxalate and water and the composition corresponded to $1.3 \text{Ti}:1.00 \text{(peroxy)}:1.3 \text{C}_2\text{O}_4:4.4 \text{H}_2\text{O}$. Further on long storage, the substance first turned yellow and finally yellowish white. The analysis of the yellowish white product showed that it was basic oxalate, having the formula $\text{TiOC}_2\text{O}_4, 3.4 \text{H}_2\text{O}$. It is thus obvious that the peroxy complex, on losing the active oxygen changes itself into basic oxalate. These studies further show that it is difficult to prepare a very pure peroxy complex whose molar ratio of $\text{Ti}:\text{O}$ (peroxy):$\text{C}_2\text{O}_4$:O (non-peroxy) is $1:1:1:1$, since it gradually loses the peroxy oxygen. Hence for carrying out physico-chemical studies the peroxy complexes had slightly lower values of active oxygen.

Determination of the Molecular Weight of the Peroxy Titanium Oxalate Complexes.—The molecular weights of the three peroxy titanium oxalates having varying amounts of active oxygen were determined cryoscopically in aqueous solutions using Beckman’s apparatus. The results are given in Table II.
TABLE II

Molecular Weights of the Peroxy Complexes by Cryoscopic Method

(a) Complexes Employed

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ti</th>
<th>O (Peroxy)</th>
<th>C₅O₄</th>
<th>O</th>
<th>H₂O</th>
<th>Approximate formula of the complex</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>1.13</td>
<td>1.0</td>
<td>1.13</td>
<td>1.18</td>
<td>3.80</td>
<td>TiO₂C₂O₄, 3.5 H₂O</td>
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<tr>
<td>B</td>
<td>1.53</td>
<td>1.0</td>
<td>1.50</td>
<td>1.68</td>
<td>5.48</td>
<td>Ti₁.₅O₂₋₅(C₂O₄)₁₋₅, 5.5 H₂O</td>
</tr>
<tr>
<td>C</td>
<td>2.09</td>
<td>1.0</td>
<td>2.10</td>
<td>2.02</td>
<td>6.64</td>
<td>Ti₂O₅(C₂O₄)₂, 6.5 H₂O</td>
</tr>
</tbody>
</table>

(b) Freezing Point Data of the above Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Weight of the complex/100 g. of H₂O (g.)</th>
<th>Lowering of F. pt. (ΔT)</th>
<th>Mole. weight of F. pt. found</th>
<th>Av. mole. weight found</th>
<th>Calculated mole. weight from the formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.3464</td>
<td>0.027</td>
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<tr>
<td></td>
<td>0.9647</td>
<td>0.077</td>
<td>231.5</td>
<td>230.0</td>
<td>231.0</td>
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<tr>
<td></td>
<td>1.1140</td>
<td>0.092</td>
<td>224.0</td>
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<tr>
<td>B</td>
<td>0.4320</td>
<td>0.028</td>
<td>287.0</td>
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<tr>
<td></td>
<td>0.8898</td>
<td>0.055</td>
<td>301.0</td>
<td>293.3</td>
<td>243.0</td>
</tr>
<tr>
<td></td>
<td>1.0200</td>
<td>0.065</td>
<td>291.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.4136</td>
<td>0.025</td>
<td>307.7</td>
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<td>1.0250</td>
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<td>302.6</td>
<td>304.1</td>
<td>437.0</td>
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<tr>
<td></td>
<td>1.3000</td>
<td>0.080</td>
<td>302.2</td>
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The results of Table II show that with complex A, the average molecular weight (230) found is practically equal to the calculated value, assuming the formula of the normal peroxy complex as TiO₂C₂O₄, 3·5 H₂O. In the
Peroxy Titanium Oxalate

293

The observed molecular weights are lower than the calculated values.

Spectral Characteristics of the Peroxy Titanium Oxalate Complexes.—The absorption spectra for the three peroxy titanium oxalate complexes (Fig. 2, complexes A, B and C) having different active oxygen content, were determined by Coleman model 14, Universal Spectrophotometer. It was found that the absorption maximum for the three complexes was at the wavelength 425 mμ. Employing a reference solution containing hydrogen peroxide and oxalic acid, transmittance (T) measurements were made for various dilutions of the three complexes at 425 mμ. It was found in all the cases that when the solution was dilute (up to 25–30 p.p.m. of Ti), Beer's law was obeyed. Further, when log T (for the three complexes at various dilutions) was plotted against peroxy oxygen present in the complexes, it was found that practically all the three curves coincided. This indicated that in the three complexes the log T was a function of the peroxy oxygen (taking same amount of Ti for the three complexes) present in the complex.

The effect of added hydrogen peroxide on the transmittance of the three complexes was then studied. The results given in Fig. 2 show that the transmittance of the three complexes remains constant when the atomic ratio of Ti:O (peroxy) reaches 1 and less. This study indicates that the normal complex TiO₂C₂O₄ is formed only when the ratio of Ti:O (peroxy) is 1:1 in all the three complexes. It may be noted here that the excess of

<table>
<thead>
<tr>
<th>Ti</th>
<th>O(PEROXY)</th>
<th>C₂O₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<tr>
<td>B</td>
<td>1.447</td>
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</tr>
<tr>
<td>C</td>
<td>4.370</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 2. Effect of Hydrogen Peroxide on per cent Transmittance of the Complexes.
oxalic acid or hydrogen peroxide over the stoichiometric amounts present in the normal peroxo complex \((\text{TiO}_2\text{C}_2\text{O}_4)\) neither altered the absorption maximum nor did they materially affect the transmittance of the normal complex for a given concentration of titanium.

**Conductivity Studies on the Peroxy Titanium Oxalate Complexes.**—The molecular conductivity of the three complexes (composition given in Fig. 3) was determined at various dilutions in aqueous solution at 25°C. The results are represented in Fig. 3. The molecular conductivity at infinite dilution is found by extrapolation of the curve A and the degree of dissociation for the normal complex is calculated. The extrapolated value for the conductivity of a normal complex at infinite dilution is found to be 110. The average dissociation constant \(K\) for the normal complex was calculated to be \(4.5 \times 10^{-2}\) while that for oxalic acid is \(K = 5.9 \times 10^{-2}\), indicating thereby that the complex has practically the same order of the degree of dissociation as that of oxalic acid. The molecular conductivity for a given titanium content is much higher in the case of the peroxo complexes B and C than for the normal peroxy complex alone. As stated later, this is due to the association between the peroxo complex and the basic oxalate producing a new complex which may have higher value for the degree of dissociation.

**Potentiometric Titration of the Peroxy Complex.**—For the potentiometric titration, 25 ml. of aqueous solution containing 322 mg. of the peroxy com-
plex $1.13 \text{ Ti}: 1.00 (\text{peroxy}): 1.20 \text{C}_2\text{O}_4: 2.97 \text{H}_2\text{O}$ were taken. The titration was carried out using the glass electrode to determine the pH of the solution, after each addition of the standard (0.1041 N) sodium hydroxide solution. $\Delta \text{pH}/\Delta \text{Vs. V}$ is plotted in Fig. 4 which shows two points of inflections, indicating the dibasic character of the complex. During the titration, the solution was clear till the first peak was passed and afterwards the solution became turbid due to the formation of yellowish white pertitanic acid. The turbidity went on increasing till the second peak was reached.

**Vapour Pressure Measurements of the Peroxy Complexes.**—Vapour pressure measurements have been employed extensively to know the nature of the water associated with the chemical compounds. During the preliminary investigation, it was found that the vapour pressure of the complex was practically a linear function of the temperature. Moreover, it was found that the complex gradually gave out small quantities of oxygen. Hence the individual pressures of these two components were determined by a slight modification of the manometric technique.

**Apparatus and Procedure.**—The all-glass apparatus consisted of a narrow cylinder A (2.5 cm. dia. $\times$ 30 cm. ht.) connected to a trap E and a mercury
manometer M as shown in Fig. 5. A Mcbain-Bakr quartz spring S, with a quartz bucket Q at the lower end, was suspended from a glass sphere H supported in the cylinder. The substance (Ca 200 mg.) was placed in the bucket Q, attached to the quartz spring S and introduced in the vessel A. The whole assembly was fitted up as shown in Fig. 5. The stopcock B was closed and the vessel A was slowly cooled in the liquid air. The stopcock was then opened and the air from the whole assembly was pumped out. The stopcock B was closed again, the refrigeration bath removed and the vessel A allowed to attain the room temperature. The vessel A was again cooled for the second time and it was noticed invariably that during the second cooling with liquid air, the powder would fly out from the bucket due to the rapid freezing of the moisture inside the tube. This difficulty, however, was avoided by admitting small quantities of dry air before cooling. After cooling the vessel A in liquid air, the system was completely evacuated for a period of half an hour to remove the residual air completely. The stopcock D was closed, the cooling bath removed and a water-bath at 2°C introduced to surround A and the total equilibrium pressure noted at this temperature. In general one hour was sufficient for the attainment of the equilibrium vapour pressure. The stopcock B was then closed and the trap E was cooled in liquid air to condense the moisture in the system between stopcocks B and D. The oxygen pressure was then noted (Fig. 6). The difference between the total pressure and the oxygen pressure gave the aqueous...
tension of the complex. In this way, the aqueous tension was determined at temperatures up to 45°C and the results are given in Fig. 7 where $1/T \times 10^4$

**Fig. 6.** Oxygen Pressure of the Peroxy Complexes at Various Temperatures.

**Fig. 7.** Effect of Temperature on the Vapour Pressure of Peroxy Complex Hydrates.
is plotted against log $P \times 10^a$. The results of analyses of the substance A, before and after the determination of the vapour pressure, showed that there was little change in the peroxo oxygen content (6·29% to 5·87% peroxo oxygen). From the vapour pressure measurements at different temperatures, the average heat of dissociation for the normal peroxo complex was found to be 15·40 K.cal./mole of water. This was calculated from the slope of the curve A. Similarly the oxygen and vapour pressures were determined for complexes B and C and the corresponding results are given in Figs. 6 and 7 respectively. The heats of dissociation for the complexes B and C were found to be 14·8 and 15·21 K.cal./mole of water respectively.

For complex A, which has got the highest peroxo oxygen content, the oxygen pressure varies from 0·12 to 0·30 mm. of mercury even when the temperature is varied from 2° to 45° C. Thus the oxygen pressure is very low as compared to the aqueous tension of the hydrate for the same range of temperature. Hence in the subsequent study, the oxygen pressure of the complex was not noted while studying the rate of loss of water on continuous evacuation at 25° C.

Rate of Loss of Water from the Normal Peroxy Complex at 25° C.—200 mg. of the sample [1·06 Ti : 1·00 (peroxy) : 1·08 C$_2$O$_4$ : 3·65 H$_2$O] was subjected to continuous evacuation and its vapour pressure noted for different water contents of the sample. The loss in weight due to evaporation of water was found out by determining the stretch of the spring (Fig. 5). The sensitivity of the spring was 63·53 mg. for a stretch of 1 cm. Since the loss of peroxo oxygen is very little as compared to that of water from the complex, the loss in weight of the complex due to the loss of peroxo oxygen is neglected. The results are given in Table III.

It is seen from Table III that the fall in vapour pressure is quite rapid till the complex has 3 moles of water, after which the fall in vapour pressure is very slow. Further, the pressure remains practically constant when the complex has about 2 moles of water per atom of titanium. The rate of loss of water at this stage is extremely slow even when evacuation is carried out for comparatively long intervals. When the dehydration of the normal peroxo complex 1·06 Ti : 1·0 (peroxy) : 1·08 C$_2$O$_4$ : 3·65 H$_2$O was carried out by keeping the substance over phosphorus pentoxide in vacuum desiccator, it was also noticed that the rate of loss of water was practically negligible, when the complex had 1·8 molecules of water per atom of titanium in the complex. It can, therefore, be concluded that the initial rapid fall in vapour pressure is due to water held in loose combination with the solid. The constancy of the composition and the vapour pressure towards the end of
the experiment indicates that the two moles of water are firmly held by the complex.

TABLE III

<table>
<thead>
<tr>
<th>Interval of evacuation in minutes</th>
<th>Moles of water retained by the complex</th>
<th>Vapour pressure mm. of Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>3.51</td>
<td>2.81</td>
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<tr>
<td>1.0</td>
<td>3.35</td>
<td>1.72</td>
</tr>
<tr>
<td>1.5</td>
<td>3.22</td>
<td>1.34</td>
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<td>2</td>
<td>3.18</td>
<td>0.89</td>
</tr>
<tr>
<td>3</td>
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<td>0.72</td>
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<td>0.12</td>
</tr>
<tr>
<td>518</td>
<td>2.15</td>
<td>0.12</td>
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Thermal Studies on the Peroxy Complexes.—The thermogravimetric behaviour of the peroxy titanium oxalate complexes was studied in the modified thermogravimetric balance and it was found that all the three complexes, having varying active oxygen contents, showed three breaks, one at 80–100°C, the second at 250°C, and the third at 320°C, when percentage loss of the substance on heating was plotted against temperature. After 320°C, the curves remained practically horizontal and the residual product on analysis was found to be titanium dioxide.

The products of decomposition formed at the transition temperatures, indicated by the thermogravimetric studies, were determined by collecting
the reactants by means of a Töpler pump. 206 mg. of the normal peroxo complex was taken in a small bulb fused with the Töpler pump. The bulb was cooled by surrounding it in liquid air and the air removed from the apparatus. The substance was then heated to 100°C, and allowed to remain at that temperature for about an hour. At this temperature, no gaseous products of decomposition were obtained. Evidently, this transition temperature indicates the absorption of heat due to loss of water from the complex. Amount of water produced could not be estimated since it was being absorbed by the phosphorus pentoxide kept in the Töpler pump. The temperature was then raised to 250°C, and the substance was allowed to remain at this temperature for about an hour, after which the rate of decomposition slowed down considerably. The gaseous products obtained were collected and analysed for oxygen, carbon monoxide and carbon dioxide. It was found that the gaseous products contained 55.4% CO₂, 38.3% CO and 6.3% O₂. The substance was finally heated to 320°C, when it completely decomposed yielding titanium dioxide and a little carbon in the residue. The gaseous products collected contained 51% CO₂ and 49% CO but no oxygen, showing that all the oxygen was liberated at 250°C.

**DISCUSSION**

1. *Molar Composition of the Normal Peroxy Complex.*—Mazzucchelli and Pontanelli¹ obtained the compound Ti₂O₃(C₂O₄)₂ which was represented as:

\[
\begin{array}{c}
\text{O} \\
\text{Ti} \\
\text{O} \\
\text{C}_2\text{O}_4
\end{array}
\]

\[\text{Ti} = \text{O}\]

In the present investigation, a similar product, having the mole ratio of Ti: O (peroxy): O: C₂O₄ as 2: 1: 2: 2 (Table I, experiments 1 to 3), is obtained, besides two more substances having the mole ratio as 1: 1: 1: 1 and 3: 2: 3: 3 respectively. The results presented in Table I show that the composition of the final product depends on the initial concentrations of the reacting constituents. When a large excess of hydrogen peroxide (Ti: per oxy O as 1: 3 and above) is present in the starting solution, the complex obtained has approximately the composition corresponding to the formula TiO₂C₂O₄.

The keeping quality of the normal peroxo complex (Fig. 1) shows that it undergoes decomposition losing peroxo oxygen gradually, while the other constituents remain unaffected. Thus, the peroxo titanium oxalate behaves like pertitanic acid on storage,² the difference being that the rate of loss of peroxo oxygen from the peroxo complex is comparatively slower than that from the pertitanic acid. It is, therefore, possible that the substance
reported by Mazzucchelli and Pontanelli is a decomposition product of the normal per oxy complex TiO$_2$C$_2$O$_4$ according to the equation:

$$4 \text{TiO}_2\text{C}_2\text{O}_4 \rightarrow 2 \text{Ti}_2\text{O}_3(\text{C}_2\text{O}_4)_2 + \text{O}_2$$

(1)

It is also possible that these authors did not employ a large excess of hydrogen peroxide in the starting solution, which resulted in obtaining a product deficient in per oxy oxygen. The substance Ti$_2$O$_3$(C$_2$O$_4$)$_2$ may be either a mixture of the normal per oxy titanium oxalate, TiO$_2$C$_2$O$_4$, and the basic oxalate, TiOC$_2$O$_4$, in equal proportions or an association complex as shown later. On long storage, the orange red per oxy titanium oxalate is transformed into the white basic oxalate.

As revealed by the spectrophotometric investigations, the three substances differing in per oxy oxygen content give the same transmittance minimum at 425 nm. Moreover, the curves represented in Fig. 2 show that the minimum percentage transmittance is obtained when the atomic ratio of Ti: O (peroxy) reached 1:1, by addition of hydrogen peroxide to any of the three substances studied. Further addition of hydrogen peroxide does not alter the transmittance of the solution. The identical behaviour of the three substances, therefore, indicates that the normal per oxy titanium oxalate complex has the ratio of Ti: O (peroxy) as 1:1. These studies also suggest that any per oxy product which does not conform to the formula TiO$_2$C$_2$O$_4$ could be considered as a mixture of the normal per oxy titanium oxalate and its deoxygenated compound. It is seen from Table I that the ratio of water:titanium is maintained at about 3.5, irrespective of the amount of per oxy oxygen in the molecule. The molar composition of the normal per oxy complex can, therefore, be represented as TiO$_2$C$_2$O$_4$, 3.5 H$_2$O.

2. Structure of the Normal Peroxy Complex.—To assign the structure to the per oxy complex, the positions of the per oxy oxygen, the water molecules and the oxalate group with respect to the titanium atom are required to be fixed from the experimental evidences. Further, the structure assigned should conform to the theoretical expectations.

A. Position of the Peroxy Oxygen.—Various tests employed to determine the nature of the per oxy oxygen show that the complex is not a per hydrate, but a true per oxy complex, having the per oxy linkage –O–O–. The pertitanic acid from which the per oxy titanium oxalate is derived is represented as,

\[
\begin{align*}
\text{O} & \xrightarrow{\text{Ti}} \text{O} \\
\text{O} & \xrightarrow{\text{OH}} \text{O} 
\end{align*}
\]
with two replaceable hydroxy groups. The peroxy linkage in the complex may, therefore, be represented as:

\[
\text{O}^\text{-}\text{Ti} = \text{C}_2\text{O}_4, \ 3\cdot5\text{H}_2\text{O}
\]

B. Position of the Molecules of Water in the Peroxy Complex.—It has been shown that the normal peroxy complex has got 3·5 moles of water, out of which 1·5 moles can be removed by dehydration in vacuum over phosphorus pentoxide. The heat of dissociation (15·4 K.cal./mole of water) for 1·5 moles of water, that are removed on evacuation, shows that the water associated with the complex molecule is combined water. The other two molecules which are difficult to remove in vacuum may be either due to (a) the co-ordinated water, or (b) partly as co-ordinated and partly as water of constitution. Accordingly, the following two are the possible structures of the peroxy complex:

\[
\begin{align*}
\text{H}_2\text{O} & | \text{O}^\text{-}\text{Ti} \text{OOC} & 1·5 \text{H}_2\text{O} & | \text{H}_2\text{O} \\
\text{H}_2\text{O} & | \text{O}^\text{-}\text{Ti} & | \text{OOC} & \text{H}_2\text{O} \\
\end{align*}
\]

(1)

\[
\begin{align*}
\text{H}_2\text{O} & | \text{O}^\text{-}\text{Ti} \text{OOC\cdotCOOH} & 1·5 \text{H}_2\text{O} \\
\text{H}_2\text{O} & | \text{O}^\text{-}\text{Ti} & | \text{OH} \\
\end{align*}
\]

(2)

According to the structure (2) the co-ordination number of titanium is five. In order to obtain a spatially symmetrical arrangement, generally, the co-ordination values of six and four are most usual with various metallic ions. It is, therefore, quite possible that a spatially symmetrical complex with co-ordination number of six as in structure (1) is produced and not as an unsymmetrical complex with co-ordination number five as in structure (2).

C. Electronic Conception and the Peroxy Complex.—According to the structure (1), titanium gains eight electrons in the formation of the co-ordination complex. Hence with the twenty-two electrons possessed by the titanium atom, the total number of electrons amount to thirty for the central atom of titanium in the complex. Titanium is expected to attain the electronic configuration of the next higher inert gas, krypton, which has 36 electrons. Cases, however, have been reported in literature where elements forming co-ordination complexes may or may not have the inert gas configuration as in the case of platinous complexes. The main significant factor in assigning the structure is that it should be symmetrical irrespective of the actual number of electrons involved. The structure (1) fulfils this requirement. The normal valency of four for titanium is also satisfied by this structure.
D. Diamagnetic Character of the Complex.—Since the electronic structure of the titanium atom in the complex falls short of the electronic configuration of the Krypton gas, one would normally expect the complex to be paramagnetic according to the rule of Welo and Baudisch. Determination of the magnetic susceptibility of the complex by Guoy balance showed that the normal peroxy complex is diamagnetic. It is likely that the electronic configuration of the central paramagnetic titanium ion has undergone redistribution under the influence of penetration due to the approach of the other atoms and molecules. Such redistribution would bring about diamagnetism in the complex.

Nature of the Complex in Aqueous Solution.—The closeness in the values for the dissociation constants of the normal peroxy complex \( K = 4.5 \times 10^{-3} \) and oxalic acid \( K_1 = 5.9 \times 10^{-2} \) suggests that the peroxy complex ionizes in a similar way as the oxalic acid in aqueous solution. This is due to the hydrolysis of the complex in aqueous solution followed by ionization according to the following scheme:

\[
\begin{align*}
\text{Ti-O}^\text{V(O)} & \quad \text{OOC} \quad + \text{H}_2\text{O} \rightarrow \\
\text{Ti-O}^\text{V(O)} & \quad \text{OOC-COOH} \\
\uparrow & \\
\text{Ti-O}^\text{V(O)} & \quad \text{OOC-CO}^\text{2-} + \text{H}^+ \\
\end{align*}
\]

Another supporting evidence for the above scheme of reactions lies in the fact that the pH of 1% aqueous solution of the peroxy complex is 2.0, showing the acid nature of the complex.

The cryoscopic determination of the molecular weight of the complexes (Table II) show that the substance A, having the mole ratio of Ti:O (peroxy):O:C\(_2\)O\(_4\) as 1:1:1:1 is nearly a pure substance while the substances B and C are contaminated with large amounts of basic oxalate. The higher molecular weights of B and C than that of the normal peroxy complex A are likely to be due to the partial association of the basic oxalate with the peroxy oxalate, according to the equation:

\[
\begin{align*}
\text{Ti-O}^\text{V(O)} & \quad \text{OOC-COOH} + \text{HOOC-COOH} \rightarrow \\
\text{Ti-O}^\text{V(O)} & \quad \text{OOC-CO}^\text{2-} + \text{H}^+ \\
\end{align*}
\]

The molecular weight of the normal peroxy complex A is very nearly equal to the theoretical value (Table III), indicating very little dissociation of the complex. This is contrary to the observation made by the conductivity studies where the degree of dissociation is 50%. The low dissociation of the substance A during the freezing point studies can be ascribed to:
(1) the low temperature employed whereby suppression of the dissociation of the complex can result, and (2) comparatively higher concentrations of the substance employed (20 times) in the freezing point experiments, which may result in the association of the complex.

The two peaks observed in the $\Delta \text{pH} / \Delta V$ vs. $V$ titration curve (Fig. 4) can be explained on the basis of the product,

$$\text{O\textsuperscript{2-}/OOC\textcdotCOOH}$$

obtained in water medium as per equation (2). When one equivalent of sodium hydroxide (15 ml.) is added to the solution containing the peroxo complex, a soluble mono-sodium complex

$$\text{O\textsuperscript{2-}/OOC\cdotCOONa}$$

is produced. With further addition of sodium hydroxide, the disodium complex hydrolyses, giving rise to $\text{Na}_2\text{C}_2\text{O}_4$ and $\text{TiO}_3$ as:

$$\text{O\textsuperscript{2-}/OOC\cdotCOONa} + \text{H}_2\text{O} \rightarrow \text{O\textsuperscript{2-}/OOC\cdotCOONa} + \text{Na}_2\text{C}_2\text{O}_4$$

(4)

The precipitation of the pertitamic acid continues till the pH of 9.45 is reached, when no more of the peroxy titanium complex will be present in the solution. Thus, the two peaks in the titration curve can be explained on the formation of the mono-sodium salt of the peroxo complex and the pertitamic acid respectively.

**Thermal Decomposition of the Peroxy Complex in Vacuum.**—The decomposition products obtained while heating the substance in Töpler pump under reduced pressure substantiates the proposed structure. The reaction (5) takes place on heating (in vacuum) followed by two side reductions (6) and (7):

$$2 \text{O\textsuperscript{2-}/OOC\cdotCOOC} \rightarrow 2\text{TiO}_2 + 2\text{CO}_2 + 2\text{CO} + \text{O}_2$$

(5)

$$2 \text{CO} + \text{O}_2 \rightarrow 2 \text{CO}_2$$

(6)

$$2 \text{CO} \rightarrow \text{CO}_2 + \text{C}$$

(7)

**Summary**

1. The method of the preparation of the normal peroxy titanium oxalate $\text{TiO}_2\text{C}_2\text{O}_4$, $3\cdot5 \text{H}_2\text{O}$ is described. If an excess of hydrogen peroxide
Peroxy Titanium Oxalate

is not maintained in the starting solution, substances with the molar compositions $\text{Ti}_2\text{O}_3(\text{C}_2\text{O}_4)_2$, 7 H$_2$O and $\text{Ti}_{1.5}\text{O}_{2.5}(\text{C}_2\text{O}_4)_{1.5}$, 5·5 H$_2$O are obtained.

2. It has been shown by the various physico-chemical studies that the substance $\text{TiO}_2\text{C}_2\text{O}_4$, 3·5 H$_2$O is a true peroxy complex, while the other two substances are mixtures of the peroxy complex and its deoxygenated product (basic oxalate TiOC$_2$O$_4$) in different proportions.

3. The keeping quality of the peroxy complex indicates that the complex loses the peroxy oxygen gradually, transforming itself into the basic oxalate.

4. Molecular weights of the three complexes described in (1) have been determined cryoscopically.

5. Conductivity of the aqueous solution of the normal peroxy complex gave the average dissociation constant $K = 4·5\times10^{-2}$.

6. Spectrophotometric investigations on the peroxy complex showed that the peroxy complex has the atomic ratio of Ti:O (peroxy) as 1:1 and the absorption maximum of the complex is at the wavelength 425 m$\mu$.

7. Potentiometric titration of the aqueous solution of the complex against sodium hydroxide indicated the dibasic character of the complex in the solution.

8. Vapour pressure data for the normal peroxy complex gave the heat of dissociation equal to 15·4 K.cal./mole of water, indicating that the water associated with the complex is combined one.

9. Oxygen pressure for the normal peroxy complex varied from 0·12 to 0·30 mm of mercury in the temperature range 2$^\circ$ to 45$^\circ$ C.

10. Dehydration studies on the normal peroxy titanium oxalate complex in vacuum showed that out of 3·5 moles of water, 1·5 moles are removed from the complex while 2 moles are retained with the complex.

11. Decomposition products obtained on heating the peroxy complex in vacuum are carbon dioxide, carbon monoxide, oxygen, water, titanium dioxide and carbon.

12. The complex has been assigned the structure

$$\begin{bmatrix}
\text{H}_2\text{O} \\
\text{O} \\
\text{H} \\
\text{OOC} \\
\text{H}_2\text{O} \\
\text{OOC} \\
\text{H}_2\text{O}
\end{bmatrix} 1·5 \text{H}_2\text{O}$$

based on various physico-chemical studies.
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REFERENCES

1. Mazzucchelli, A. and Potanelli
2. Kharkar, D. P. and Patel, C. C.
3. Weissler, A.
4. Kolthoff, I. M and Sandell, E. B.
5. Abel, E.
7. Krauss, F. and Oettner, C
8. Llebhafsky, H. A.
10. Ephraim, F.
11. Welo, L. A. and Baudisch, O.
12. Guoy, M.
13. Pauling, L.

Att. Acad Lincei, 1908, 18(1), 518.
Ibid., 1934, 221, 25.
Chemistry and Industry, April 28, 1956, pp. 300.
Compt. rend., 1889, 109, 935.
J A.C.S., 1931, 53, 1367