CHAPTER I

PART I: Method of preparation and preliminary study on the water decomposition product of blue acid extracted with ethyl acetate.

PART II: Method of preparation and preliminary study on the water decomposition product of blue acid extracted with ether.
Pillai and Rai have proved that water decomposition product of blue acid extracted by ethyl acetate is $\text{Cr}_2\text{(O}_2\text{OO)}_3$, i.e., chromium peroxy dichromate. I prepared the above compound and studied its properties. Experimental details regarding its preparation are given below:

**EXPERIMENTAL:**

**Preparation of blue peroxy chromic acid:**

Analar samples of potassium dichromate and sulphuric acid were taken. Ethyl acetate was purified by distillation. The blue peroxy chromic acid was prepared by adding 35 ml. of 20 volume (6%) hydrogen peroxide to a mixture of 5% (w/v) solution of potassium dichromate, sulphuric acid (2M, 7.5 ml.) and ethyl acetate (100 ml.). All the solutions were cooled in a refrigerator before mixing. The blue solution went into the ethyl acetate layer. This was carefully separated and was throughly washed for four or five times with ice cold distilled water. The blue solution was separated finally and taken into Jena glass bottle and kept in the ice.

(A) **Oxidation power of the blue peroxy chromic acid (Iodometric Titration):**

A titration flask containing neutral aqueous solution of potassium iodide was taken and the blue acid (5 ml.) was withdrawn in to it.
(a) Oxidation power of the first stage:

Liberated iodine in the first flask was titrated with standard solution of sodium thiosulphate (N/20) using starch solution as an indicator. The end point was marked when the colour of the solution change from blue to pale yellow (not green).

(b) Oxidation power of the second stage:

After the first state titration 2N sulphuric acid (10 ml.) was added to the same reaction mixture. The further quantity of the liberated iodine was titrated against the same standard sodium thiosulphate solution. This time the colour of the solution at the end point was characteristic green.

Decomposition of blue acid in water:

Three titration flasks, each containing about 25 ml. of distilled water were taken and the blue compound (2 ml.) was withdrawn into each. The blue compound decomposes after about an hour and colour of the solution becomes yellow brown.

(B) Oxidation power of the water-decomposition product:

After the complete decomposition, aqueous solution of potassium iodide was added to one of the above flasks.

(a) Oxidation power of the first stage:

Immediately after the addition of potassium iodide 2 ml. of standard solution of sodium thiosulphate was added and the covered flask was kept for an hour. The liberated iodine in the
above flask was titrated as above. The end point was marked when colour of the solution changed from blue to pale yellow.

(b) Oxidising power of the second stage:

After the first stage titration, 2N sulphuric acid (10ml.) was added to the above reaction mixture and further quantity of the liberated iodine was titrated as usual.

(c) Oxidation power of the water decomposition product after oxidation:

To the second flask containing the water decomposition product a small amount of sodium hydroxide and 5 ml. of 100 vol. (30%) hydrogen peroxide were added and the mixture was carefully boiled. The excess of hydrogen peroxide was decomposed by prolonged boiling till the frothing had ceased and the flask was then cooled to room temperature. The colour of the solution was pale-yellow. It was acidified with 2N sulphuric acid, till the colour of the solution changed to dark yellow. To this acidified solution potassium iodide was added and its oxidation power was determined as given before.

(d) Oxidation power of the decomposition product in water after boiling and cooling:

The water decomposition product contained in the third flask was boiled for about half an hour and then it was cooled to room temperature. Aqueous potassium iodide was added to it and
after acidifying, its oxidising power was determined as before.

From these observations different oxidising power and their ratios were calculated as shown in the table No. 1.

Note: After seeing the first and second stage of blue peroxy chromic acid, rest of blue acid was decomposed in 30 ml. of distilled water and kept at a cold place. This decomposition product was used in all the experiments.

REFERENCE

TABLE No. 1

OXIDISING POWER OF BLUE PEROXY CHROMIC ACID AND ITS WATER DECOMPOSITION PRODUCT.

5% (v/v) K₂Cr₂O₇ solution = 75 ml.  
Sulphuric acid = 7.5 ml.  
Hydrogen peroxide = 35 ml.  
Ethyl acetate = 100 ml.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Blue compound</th>
<th>Water decomposition product</th>
<th>Water decomposition</th>
<th>R</th>
<th>A</th>
<th>T</th>
<th>I</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First stage</td>
<td>Second stage</td>
<td>Boiled</td>
<td>a/b</td>
<td>a/b</td>
<td>d/c</td>
<td>c/d</td>
<td>c/d</td>
<td>f/b</td>
</tr>
<tr>
<td></td>
<td>First stage</td>
<td>Second stage</td>
<td>After oxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>b</td>
<td>c</td>
<td>d</td>
<td>e</td>
<td>f</td>
<td>g</td>
<td>h</td>
<td>i</td>
<td>j</td>
</tr>
<tr>
<td>1</td>
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<td>21.00</td>
<td>5.20</td>
<td>15.60</td>
<td>16.60</td>
<td>21.20</td>
<td>0.65</td>
<td>2.2</td>
<td>3</td>
</tr>
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<td>2</td>
<td>7.20</td>
<td>12.80</td>
<td>3.20</td>
<td>9.60</td>
<td>9.60</td>
<td>12.80</td>
<td>0.66</td>
<td>2.0</td>
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</tr>
<tr>
<td>3</td>
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<td>19.20</td>
<td>4.20</td>
<td>14.40</td>
<td>14.40</td>
<td>19.20</td>
<td>0.66</td>
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<td>3</td>
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<td>4</td>
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<td>22.80</td>
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<td>23.80</td>
<td>0.56</td>
<td>2.0</td>
<td>3</td>
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</table>

(continued)
Prakash, S., & Rai, R.C., (loc. cit.) have shown that water decomposition product of blue acid extracted by ether is \( \text{Cr}_2(\text{Cr}_2\text{O}_7) \), i.e., chromium dichromate. I prepared the above compound and studied its properties. Experimental details regarding its preparation are given below:

**Experimental:**

**Preparation of the blue peroxo chromic acid:**

Analar sample of potassium dichromate, sulphuric acid were taken. Ether was purified to remove its peroxide impurities by shaking it with a concentrated solution of ferrous sulphate and then distilled it. The blue peroxo chromic acid prepared by adding 35 ml. of 20 volume (6%) of hydrogen peroxide to a mixture of 5% (v/v) potassium dichromate (75 ml.) solution, sulphuric acid (2 M, 7.5 ml.) and ether (100 ml.). All the solutions were cooled in a refrigerator before mixing. The blue solution went into the ether layer. This was carefully separated and was thoroughly washed four to five times with ice cold distilled water. The blue solution was separated finally and taken into Jena glass bottle and kept in the ice.

(A) **Oxidation power of the blue peroxo chromic acid (iodometric titration):**

A titration flask containing neutral aqueous solution of potassium iodide was taken and the blue compound (5 ml.) was
withdrawn in to it.

(a) Oxidation power of the first stage:

The liberated iodine in the first flask was titrated with standard solution of sodium thiosulphate (N/20) using starch solution as an indicator. The end point was marked when the colour of the solution changed from blue to pale yellow (not green).

(b) Oxidation power of the second stage:

After the first stage titration, the above reaction mixture was acidified with sulphuric acid (2N) and then further quantity of the liberated iodine was titrated against the same standard solution of sodium thiosulphate. This time the colour of the solution at the end point was characteristic green.

Decomposition of blue peroxy dichromate in water:

Three titration flasks, each containing about 50 ml. of distilled water were taken and blue compound 5 ml. was withdrawn into each. The blue compound decomposes after about an hour and the colour of the solution becomes yellow brown.

(B) Oxidation power of the water decomposition product:

After the complete decomposition, to one of the above flasks neutral aqueous solution of potassium iodide was added. It was seen that no iodine liberated in the aqueous medium. Then 2 N sulphuric acid (10 ml.) was added to it, and the liberated iodine was titrated with the standard solution of sodium thiosulphate.
Oxidation power of the water decomposition product after its oxidation:

(b) To the second flask containing the water decomposition product, a small amount of sodium hydroxide and 5 ml. of 100 vol. hydrogen peroxide (30%) were added and the mixture was carefully boiled. The excess of hydrogen peroxide was decomposed by prolonged boiling till the forthing had ceased and the flask was then cooled to room temperature. The colour of the solution was pale yellow. It was acidified with 2N sulphuric acid, when the colour of the solution changed to dark yellow. To this acidified solution potassium iodide was added and oxidation power was determined as before.

(c) Oxidation power of the water decomposition product after boiling and cooling:

The water decomposition product contained in the third flask was boiled for about half an hour and then it was cooled to room temperature. The aqueous potassium iodide was added to it and after acidification its oxidising power was determined as before.

From these observations different oxidising powers and their different ratios were calculated as shown in the table No. 2.

After seeing the first and second stage of the blue peroxo chromic acid, the rest of the blue acid was decomposed in 30 ml. of distilled water. The decomposition product was used in all the experiments.
**TABLE No. 2**

**OXIDISING POWER OF BLUE PEROXY CHROMIC ACID AND ITS WATER DECOMPOSITION PRODUCT**

- $5\% (v/v) \text{K}_2\text{Cr}_2\text{O}_7$ solution = 75 ml.
- Sulphuric acid = 7.5 ml.
- Hydrogen peroxide = 35 ml.
- Ether = 100 ml.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Volume in ml. of sodium thiosulphate used</th>
<th>Blue compound</th>
<th>Water decomposition product</th>
<th>Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>First stage</td>
<td>Second stage</td>
<td>Without boiling</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>a</td>
<td>b</td>
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</tr>
<tr>
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<td></td>
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<td>b</td>
<td>c</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
</tr>
</tbody>
</table>

- a/b, a/b, d/b, a/b