CHAPTER III

Gravimetric study of decomposition products of ethereal blue perchromate prepared with sulphuric acid, with and without the application of ion-exchange resins.
The ethereal blue perchromate decomposes differently under different conditions, yielding different products. No serious attempt has, however, yet been made to ascertain the composition of and to assign chemical formulae to the various decomposition products of ethereal blueperchromate on results obtained by gravimetric studies. Therefore, I thought it proper to undertake the study of composition gravimetrically of the various decomposition products, the water, the open bottle and the closed bottle decomposition products of ethereal blue perchromate unexchanged and exchanged with the help of ion-exchange resins.

EXPERIMENTAL:

Several samples of blue perchromate were prepared by mixing ice-cold solutions of 5% w/v $\text{K}_2\text{Cr}_2\text{O}_7$ (50 ml.), 2N sulphuric acid (10 ml.) and 6% hydrogen peroxide (varying volumes). The blue perchromate thus formed was then extracted with ice-cold ethyl ether (100 ml.). The ethereal blue solution was separated, washed several times with ice-cold distilled water and placed in a tightly stoppered flask in the refrigerator in order to freeze out water. After about 2 to 3 hours it was transferred to previously dried flask and kept in ice to proceed with the studies.

PREPARATION OF DECOMPOSITION PRODUCTS:

(1) Water decomposition product: 25 ml. each of the samples of ethereal blue perchromate was withdrawn separately into a number of Erlenmeyer flasks each of which contained about 100 ml. distilled
water, and left for more than four hours for complete decomposition. This water decomposition product was made up to 250 ml. in a measuring flask by adding distilled water.

(2) **Open bottle and the closed bottle decomposition products:**

25 ml. each of the samples of blue perchromate was allowed to decompose in the two previously dried Erlenmeyer flasks under unstoppered (open bottle) conditions and tightly stoppered (closed bottle) conditions. The open bottle contents required about 14 to 16 hours at 10 to 15°C for complete decomposition till a brown residue was left in the flask. The closed bottle contents were left as such for about 40 to 48 hours for complete decomposition. The colourless ethereal layer and the brown residue at the bottom of the flask showed the completeness of the decomposition of the blue compound. The colourless ethereal layer was then decanted off.

The open bottle and the closed bottle decomposition products were dissolved in water after adding few drops of N. HNO₃ and were made up to 250 ml. in the measuring flasks separately in each case.

**Quantitative estimation of the various decomposition products:**

(a) **Unexchanged:** The gravimetric estimations of oxidised and unoxidised decomposition products were made from the above 250 ml. solution. In each case 25 ml. each of the decomposition products (water, open bottle and closed bottle) of each sample was withdrawn each time in the two 250 ml. pyrex beakers separately and diluted to
100 ml. The contents of one of the beakers were oxidised with 30% hydrogen peroxide (5 ml.) in an alkaline medium, N NaOH (10 ml.) in each case. The excess of hydrogen peroxide was then removed by prolonged boiling. The oxidised yellow coloured solution was found to be sodium chromate and was estimated gravimetrically as such while the unoxidised solution was estimated gravimetrically in two steps, i.e., before oxidation and after oxidation as follows:

The oxidised and unoxidised solutions were acidified with dilute acetic acid (A.R.) until they were distinctly acidic and boiled. -10 ml. of 4% hot solution of lead nitrate (A.R.) was added drop by drop with the help of a pipette again boiled gently for about 10 minutes, cooled and filtered through sintered glass crucible, washed thoroughly with hot water, dried at 120° to constant weight. The filtrate and washings of the unoxidised solution were collected, boiled and excess of lead was removed as lead sulphate. After the removal of lead from the concentrated filtrate cationic chromium was precipitated as chromium hydroxide, filtered, washed with hot water and then transferred to a 250 ml. pyrex beaker and oxidised with 30% hydrogen peroxide in an alkaline medium (NaOH). After removing the excess of hydrogen peroxide by prolonged boiling, it was precipitated as PbCrO₄ and estimated as described above. The same procedure of precipitation and estimation was repeated twice or thrice.

(b) Exchanged with the help of ion-exchange resins: Several columns (6/120 mm.) were prepared for the different cation exchangers and washed thoroughly with distilled water. Cations and anions were
separated from the 25 ml. of each of the decomposition products solutions (made up to 250 ml.) by exchanging through the columns of resins. Effluents containing anions were then estimated as such gravimetrically, as lead chromate by the method described above. The cations were then eluted by 60 ml. sulphuric acid, 30 ml. each of the 2N and 4 N sulphuric acid, by fraction of 10 ml. of 2N and 4N H$_2$SO$_4$ each time. The eluant was concentrated by boiling and cationic chromium was precipitated as chromium hydroxide$^3$, filtered, washed with hot water several times, and estimated as PbCrO$_4$ after oxidation by the usual methods of oxidation as given above.

The results of investigations are recorded in the following tables:
### Table 3.1
WATER DECOMPOSITION PRODUCT

Vol. (ml.) water decomposition product estimate (unexchanged & exchanged) each time = 20 ml.

Drop rate = 10 to 12 per minute.

Column = (6/120 mm.).

<table>
<thead>
<tr>
<th>Vol. of ( \text{H}_2\text{O}_2 ) used (ml.)</th>
<th>UneXChAnGED ( \text{Wt. of chromate as lead chromate in gms.} )</th>
<th>Cation Exchangers</th>
<th>EXChAnGED ( \text{Wt. of chromate as lead chromate(gm.)} )</th>
<th>RatIOS</th>
<th>c</th>
<th>a</th>
<th>c</th>
<th>d</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>unoxidised</td>
<td>Filtrate of (a) after oxidation</td>
<td>oxidation</td>
<td>Effluent Elutriant</td>
<td>Unoxi- Oxidi- Oxidi-</td>
<td>a</td>
<td>b</td>
<td>d+f</td>
<td>f</td>
</tr>
<tr>
<td>10</td>
<td>0.0824</td>
<td>0.0272</td>
<td>0.1099</td>
<td>Dowex 50W -X8</td>
<td>0.0802</td>
<td>0.0814</td>
<td>0.0280</td>
<td>1.33</td>
<td>3.03</td>
</tr>
<tr>
<td>10</td>
<td>0.0789</td>
<td>0.0280</td>
<td>0.1096</td>
<td>IRC-50H Amberlite</td>
<td>0.0797</td>
<td>0.0801</td>
<td>0.0278</td>
<td>1.38</td>
<td>2.87</td>
</tr>
<tr>
<td>15</td>
<td>0.1296</td>
<td>0.0469</td>
<td>0.1805</td>
<td>Dowex 50W -X8</td>
<td>0.1304</td>
<td>0.1318</td>
<td>0.0449</td>
<td>1.39</td>
<td>2.76</td>
</tr>
<tr>
<td>15</td>
<td>0.1314</td>
<td>0.0457</td>
<td>0.1794</td>
<td>IRC-50H Amberlite</td>
<td>0.1290</td>
<td>0.1292</td>
<td>0.0440</td>
<td>1.36</td>
<td>2.87</td>
</tr>
<tr>
<td>20</td>
<td>0.1554</td>
<td>0.0523</td>
<td>0.2088</td>
<td>Dowex-50W -X8</td>
<td>0.1549</td>
<td>0.1562</td>
<td>0.0516</td>
<td>1.34</td>
<td>2.96</td>
</tr>
</tbody>
</table>
### TABLE 3.2

**OPEN BOTTLE DECOMPOSITION PRODUCT**

Vol. (ml.) of open bottle decomposition product estimated (unexchanged & exchanged) each time: 20 ml.

Drop rate: 10 to 12 per minute. Column: (6/120 mm.).

<table>
<thead>
<tr>
<th>Vol. of H₂O₂ used (ml.)</th>
<th>UNEXCHANGED</th>
<th>EXCHANGED</th>
<th>RATIO S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt. of chromate as lead chromate in gms.</td>
<td>Effluent Elutriant Wt. of chromate as lead chromate (gms.)</td>
<td>g</td>
</tr>
<tr>
<td></td>
<td>Unoxidised Filtrate of After oxidation.</td>
<td>Unoxi-Oxidised Sediment</td>
<td>a</td>
</tr>
<tr>
<td>a</td>
<td>b</td>
<td>c</td>
<td>d</td>
</tr>
<tr>
<td>10</td>
<td>0.0874</td>
<td>0.0580</td>
<td>0.1504</td>
</tr>
<tr>
<td>20</td>
<td>0.0863</td>
<td>0.0569</td>
<td>0.1502</td>
</tr>
<tr>
<td>15</td>
<td>0.0990</td>
<td>0.0652</td>
<td>0.1638</td>
</tr>
<tr>
<td>15</td>
<td>0.0820</td>
<td>0.0524</td>
<td>0.1368</td>
</tr>
<tr>
<td>20</td>
<td>0.1215</td>
<td>0.0802</td>
<td>0.2038</td>
</tr>
<tr>
<td>Vol. of H$_2$O$_2$ used (ml.)</td>
<td>UNEXCHANGED</td>
<td>EXCHANGED</td>
<td>RATIOS</td>
</tr>
<tr>
<td>----------------------------</td>
<td>--------------</td>
<td>------------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td>Wt. of chromate as lead chromate in gms.</td>
<td>Effluent Elutriant Wt. of chromate as lead chromate (gm.)</td>
<td>c-a-c-d-a</td>
</tr>
<tr>
<td></td>
<td>Unoxidised.</td>
<td>Cation Exchangers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Filtrate of (a)</td>
<td>Oxidation after oxidation.</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.0780</td>
<td>0.0769</td>
<td>0.1578</td>
</tr>
<tr>
<td>10</td>
<td>0.0802</td>
<td>0.0796</td>
<td>0.1584</td>
</tr>
<tr>
<td>15</td>
<td>0.0870</td>
<td>0.0805</td>
<td>0.1692</td>
</tr>
<tr>
<td>15</td>
<td>0.0890</td>
<td>0.0810</td>
<td>0.1783</td>
</tr>
<tr>
<td>20</td>
<td>0.1219</td>
<td>0.1200</td>
<td>0.2444</td>
</tr>
</tbody>
</table>
From the various ratios of the tables 3.1, 3.2 and 3.3, it is evident that the amounts of chromium in the cationic and anionic portions of the water, the open and the closed bottle decomposition products are present in the ratio 1:3, 2:3 and 1:1 respectively. Therefore, the formulae, $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$, $\text{Cr}_2(\text{CrO}_4)_3$ and $\text{Cr}(\text{CrO}_4)$ for water, open and closed bottle decomposition products of ethereal blue perchromate are confirmed gravimetrically.

**REFERENCES**

