CHAPTER IV

EXPERIMENTAL DATA, SUMMARY OF RESULTS OF
REDUCTION OF CHROMIC ACID BY MALIC ACID
IN AQUEOUS SUCCINIC ACID MEDIUM.
KINETIC STUDY OF REDUCTION OF CHROMIC ACID BY MALIC ACID IN AQUEOUS SUCCINIC ACID MEDIUM

As stated earlier, the author has also studied the kinetics of reduction of chromic acid by malic acid in aqueous succinic acid medium. The author has ascertained that succinic acid does not react with either chromic or malic acid and also with other acids under experimental conditions of the study.

All the chemicals used were either B.D.H. Analar or R/5 Merck C.R. Grade. The experiments were carried out at 35°C with 0.2 and 0.3 N malic acid and 0.008 N chromic acid, varying succinic acid concentration from 0.0 to 0.5 N. The reaction was followed iodometrically by taking out known aliquots of reaction mixture at definite intervals and quenching the reaction with KI - H₂SO₄ and the liberated iodine was titrated by hypo. The Ostwald's isolation method was followed for kinetic measurements.

Tables IA, IB and II give the comparison of the reaction kinetics in absence and presence of succinic acid.
### TABLE IA
Temperature 35°C

<table>
<thead>
<tr>
<th>Malic acid 0.2 N</th>
<th>Succinic acid 0.00 N</th>
<th>Chromic acid 0.005 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>time (min.)</td>
<td>ml. of hypo (a-x)</td>
<td>K₁</td>
</tr>
<tr>
<td>0</td>
<td>11.35</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>9.30</td>
<td>0.006646</td>
</tr>
<tr>
<td>50</td>
<td>8.05</td>
<td>0.006777</td>
</tr>
<tr>
<td>70</td>
<td>7.10</td>
<td>0.006704</td>
</tr>
<tr>
<td>90</td>
<td>6.20</td>
<td>0.006720</td>
</tr>
<tr>
<td>110</td>
<td>5.45</td>
<td>0.006678</td>
</tr>
<tr>
<td>130</td>
<td>4.80</td>
<td>0.006624</td>
</tr>
<tr>
<td>150</td>
<td>4.10</td>
<td>0.006789</td>
</tr>
<tr>
<td>180</td>
<td>3.35</td>
<td>0.006779</td>
</tr>
</tbody>
</table>

Average .. 0.006727 min⁻¹

---

### TABLE IB
Temperature 35°C

<table>
<thead>
<tr>
<th>Malic acid 0.2 N</th>
<th>Succinic acid 0.3 N</th>
<th>Chromic acid 0.005 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>time (min.)</td>
<td>ml. of hypo (a-x)</td>
<td>K₁</td>
</tr>
<tr>
<td>0</td>
<td>12.10</td>
<td>-</td>
</tr>
<tr>
<td>30</td>
<td>9.78</td>
<td>0.007199</td>
</tr>
<tr>
<td>50.5</td>
<td>9.35</td>
<td>0.007176</td>
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<tr>
<td>70</td>
<td>7.25</td>
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<td>6.30</td>
<td>0.007236</td>
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<tr>
<td>110</td>
<td>5.50</td>
<td>0.007143</td>
</tr>
<tr>
<td>130</td>
<td>4.85</td>
<td>0.007013</td>
</tr>
<tr>
<td>150</td>
<td>4.20</td>
<td>0.007046</td>
</tr>
<tr>
<td>180</td>
<td>3.40</td>
<td>0.007042</td>
</tr>
</tbody>
</table>

Average .. 0.007144 min⁻¹
### TABLE II
Temperature 35°C
Chromic acid 0.005 N

<table>
<thead>
<tr>
<th>No.</th>
<th>Malic acid (N)</th>
<th>Succinic acid (N)</th>
<th>$K_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>0.00</td>
<td>0.006727</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.30</td>
<td>0.007144</td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>0.50</td>
<td>0.007168</td>
</tr>
<tr>
<td>4</td>
<td>0.3</td>
<td>0.00</td>
<td>0.006180</td>
</tr>
<tr>
<td>5</td>
<td>0.3</td>
<td>0.30</td>
<td>0.006245</td>
</tr>
<tr>
<td>6</td>
<td>0.3</td>
<td>0.50</td>
<td>0.006267</td>
</tr>
</tbody>
</table>

Order with respect to malic acid:

(a) From 1 and 4  1.83
(b) From 2 and 5  1.76
(c) From 3 and 6  1.76

Tables IIIA, IV, V, V, and VIA give the kinetic data and tables IIB, IVB, VB, and VIB illustrate the effect of sulphuric acid, hydrochloric acid, acetic acid and phosphoric acid on the reaction rate in absence and presence of succinic acid. For brevity only few sets have been given.
### EFFECT OF SULPHURIC ACID

**TABLE IIIA**
Temperature 35°C

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>ml. of hypo (a-x)</th>
<th>K₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13.10</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>10.25</td>
<td>0.016365</td>
</tr>
<tr>
<td>30</td>
<td>8.20</td>
<td>0.016821</td>
</tr>
<tr>
<td>45</td>
<td>6.45</td>
<td>0.016737</td>
</tr>
<tr>
<td>60</td>
<td>5.00</td>
<td>0.016055</td>
</tr>
<tr>
<td>75</td>
<td>3.95</td>
<td>0.015987</td>
</tr>
<tr>
<td>86</td>
<td>3.25</td>
<td>0.016176</td>
</tr>
</tbody>
</table>

Average... 0.015989 min⁻¹

**TABLE IIIB**
Temperature 35°C

<table>
<thead>
<tr>
<th>No.</th>
<th>Sulphuric acid (N)</th>
<th>Succinic acid (N)</th>
<th>K₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.00</td>
<td>0.015847</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.30</td>
<td>0.015812</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.50</td>
<td>0.015989</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.00</td>
<td>0.039934</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>0.30</td>
<td>0.039934</td>
</tr>
<tr>
<td>6</td>
<td>0.5</td>
<td>0.50</td>
<td>0.039796</td>
</tr>
<tr>
<td>7</td>
<td>1.0</td>
<td>0.00</td>
<td>0.054604</td>
</tr>
<tr>
<td>8</td>
<td>1.0</td>
<td>0.30</td>
<td>0.054684</td>
</tr>
<tr>
<td>9</td>
<td>1.0</td>
<td>0.50</td>
<td>0.054696</td>
</tr>
</tbody>
</table>
### TABLE IVa
**Temperature 35°C**

<table>
<thead>
<tr>
<th>time (min.)</th>
<th>ml. of hypo (a-x)</th>
<th>Malic acid 0.2 N</th>
<th>Succinic acid 0.3 N</th>
<th>Hydrochloric acid 0.1 N</th>
<th>( K_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.70</td>
<td></td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>10.8</td>
<td>7.60</td>
<td></td>
<td></td>
<td></td>
<td>0.023837</td>
</tr>
<tr>
<td>20</td>
<td>6.20</td>
<td></td>
<td></td>
<td></td>
<td>0.022865</td>
</tr>
<tr>
<td>30</td>
<td>4.80</td>
<td></td>
<td></td>
<td></td>
<td>0.023444</td>
</tr>
<tr>
<td>40</td>
<td>3.75</td>
<td></td>
<td></td>
<td></td>
<td>0.023967</td>
</tr>
<tr>
<td>50</td>
<td>2.95</td>
<td></td>
<td></td>
<td></td>
<td>0.023813</td>
</tr>
</tbody>
</table>

Average: 0.023349 min.⁻¹

### TABLE IVb
**Temperature 35°C**

<table>
<thead>
<tr>
<th>No.</th>
<th>Hydrochloric acid (N)</th>
<th>Succinic acid (N)</th>
<th>( K_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.10</td>
<td>0.00</td>
<td>0.022684</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.30</td>
<td>0.023549</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>0.50</td>
<td>0.027928</td>
</tr>
<tr>
<td>4</td>
<td>0.48</td>
<td>0.00</td>
<td>0.031251</td>
</tr>
<tr>
<td>5</td>
<td>0.48</td>
<td>0.50</td>
<td>0.030030</td>
</tr>
<tr>
<td>6</td>
<td>0.48</td>
<td>0.50</td>
<td>0.028182</td>
</tr>
<tr>
<td>7</td>
<td>0.50</td>
<td>0.00</td>
<td>0.030100</td>
</tr>
<tr>
<td>8</td>
<td>0.50</td>
<td>0.30</td>
<td>0.028669</td>
</tr>
<tr>
<td>9</td>
<td>0.50</td>
<td>0.50</td>
<td>0.027866</td>
</tr>
<tr>
<td>10</td>
<td>1.00</td>
<td>0.00</td>
<td>0.019093</td>
</tr>
<tr>
<td>11</td>
<td>1.00</td>
<td>0.30</td>
<td>0.018228</td>
</tr>
<tr>
<td>12</td>
<td>1.00</td>
<td>0.50</td>
<td>0.017466</td>
</tr>
</tbody>
</table>
### EFFECT OF ACETIC ACID

**TABLE V-A**

**Temperature 35°C**

<table>
<thead>
<tr>
<th>Malic acid 0.2 N</th>
<th>Succinic acid 0.3 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrome acid 0.005 N</td>
<td>Acetic acid 0.5 N</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>time (min.)</th>
<th>ml. of hypo (a-x)</th>
<th>( K_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>12.85</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>11.55</td>
<td>0.007123</td>
</tr>
<tr>
<td>30</td>
<td>10.40</td>
<td>0.007054</td>
</tr>
<tr>
<td>45</td>
<td>9.30</td>
<td>0.007155</td>
</tr>
<tr>
<td>60</td>
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<td>0.007169</td>
</tr>
<tr>
<td>90</td>
<td>6.75</td>
<td>0.007153</td>
</tr>
</tbody>
</table>

Average .. \( 0.0071397 \) min. \(^{-1}\)

### TABLE V-B

**Temperature 35°C**

<table>
<thead>
<tr>
<th>Malic acid 0.2 N</th>
<th>Succinic acid 0.3 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chrome acid 0.005 N</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Acetic acid (N)</th>
<th>Succinic acid (N)</th>
<th>( K_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.00</td>
<td>0.0071190</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0.30</td>
<td>0.0071397</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>0.50</td>
<td>0.0071468</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>0.00</td>
<td>0.0073189</td>
</tr>
<tr>
<td>5</td>
<td>1.0</td>
<td>0.30</td>
<td>0.0073225</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>0.50</td>
<td>0.0073212</td>
</tr>
<tr>
<td>7</td>
<td>2.0</td>
<td>0.00</td>
<td>0.0082056</td>
</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>0.50</td>
<td>0.0082324</td>
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<tr>
<td>9</td>
<td>2.0</td>
<td>0.50</td>
<td>0.0082217</td>
</tr>
</tbody>
</table>
## EFFECT OF PHOSPHORIC ACID

### TABLE VI-A

Temperature 35°C

<table>
<thead>
<tr>
<th>Malic acid 0.2 N</th>
<th>Succinic acid 0.5 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromic acid 0.005 N</td>
<td>Phosphoric acid 0.1 N</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>time (Min.)</th>
<th>ml. of hypo (a-x)</th>
<th>$k_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.10</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>6.70</td>
<td>0.00734617</td>
</tr>
<tr>
<td>40</td>
<td>7.55</td>
<td>0.0072774</td>
</tr>
<tr>
<td>60</td>
<td>6.50</td>
<td>0.0073465</td>
</tr>
<tr>
<td>80</td>
<td>5.60</td>
<td>0.0073719</td>
</tr>
<tr>
<td>100</td>
<td>4.95</td>
<td>0.0071384</td>
</tr>
<tr>
<td>120</td>
<td>4.30</td>
<td>0.0071163</td>
</tr>
</tbody>
</table>

Average $= 0.0072843$ min$^{-1}$

### TABLE VI-B

Temperature 35°C

<table>
<thead>
<tr>
<th>Malic acid 0.2 N</th>
<th>Chromic acid 0.005 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid 0.1 N</td>
<td>Succinic acid 0.5 N</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Phosphoric acid (N)</th>
<th>Succinic acid (N)</th>
<th>$k_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>0.00</td>
<td>0.00733808</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.30</td>
<td>0.0073112</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>0.50</td>
<td>0.0072345</td>
</tr>
<tr>
<td>4</td>
<td>0.5</td>
<td>0.00</td>
<td>0.0064592</td>
</tr>
<tr>
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<td>0.5</td>
<td>0.30</td>
<td>0.0064932</td>
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<td>0.0064216</td>
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<td>0.00</td>
<td>0.0048432</td>
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<td>8</td>
<td>1.0</td>
<td>0.30</td>
<td>0.0048408</td>
</tr>
<tr>
<td>9</td>
<td>1.0</td>
<td>0.50</td>
<td>0.0048093</td>
</tr>
</tbody>
</table>
SUMMARY OF RESULTS AND DISCUSSION

The data in tables IA and IB clearly show that the values of $K_1$ are fairly constant indicating the order of the reaction in absence and presence of succinic acid, is one, with respect to chromic acid. The order with respect to malic acid, both in presence and absence of succinic acid, calculated from table II works out to be two. Thus the total order of the reaction in both the cases, is three. These findings are in close agreement with Dharmadhikari's observations with chromic-malic acid system. The data in table II, make it evident that the velocity coefficient is slightly greater in presence of succinic acid.

Various workers have observed that the acids have catalytic effect on the rate of different reactions. Dhar has studied the effect of sulphuric acid on the reduction of chromic acid. Rai and Mahajani have found that in chromic-exallic acid system, at lower concentrations of $H_2SO_4$ reaction rate increases but at higher concentrations of $H_2SO_4$, the effect is reversed. Dharmadhikari and Mahajani have observed in chromic-malic acid system, that reaction rate increases with increase in concentration of $H_2SO_4$. The data in table IIIB make it evident that the rate of the reaction between malic acid and chromic acid increases with increase in the concentration of $H_2SO_4$ both in the absence and the presence of succinic acid. The values of $K_1$ in both the cases are nearly
the same. Evidently succinic acid does not produce any effect on the rate of the reaction.

On the other hand, the value of $K_1$ in table IV-B show that in case of hydrochloric acid, at lower concentrations up to 0.48 N, the reaction velocity increases but above 0.48 N the effect is reversed. Similar observations on chromic-malic acid and chromic - oxalic acid systems, have been reported by Dharmadhikari$^2$ and Rai$^9$ respectively. The values of $K_1$ in table IV-B indicate that the retardation in the reaction rate is slightly more in presence of succinic acid.

It is seen from table V-B that the presence of succinic acid in the reaction mixture has little effect in enhancing the effect due to acetic acid alone. Phosphoric acid has a retarding effect on the rate of the reaction. It is evident from table VI-B that succinic acid cause a slightly greater retarding effect than phosphoric acid alone.

The kinetic data in tables III-A, IV-A, V-A and VI-A show that the order of reaction with respect to chromic acid is one, in the presence of all the acids.

Succinic acid is a weak acid. Obviously its degree of ionisation in presence of malic and other acids is very small i.e. it must be existing mostly as neutral molecules HOOC-CH$_2$-CH$_2$-COOH. Its contribution towards the acidity of the medium is negligible. Attempts were made to see if the addition of succinic acid made a significant change in the
pH value of the reaction mixture. The Phillips pH-Meter, used for this purpose, did not show any measurable change.

As the observed effects in the presence of succinic acid are very small, it can be concluded, that neutral succinic acid molecules (even when present in larger concentrations), do not affect the rate of the reaction.

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