Ion-pair Formation Studies: Part VI—Effect of Ion-pairs on Kinetics of Reaction Between Sodium Iodoacetate & Sodium Thiosulphate

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The kinetics of reaction between sodium iodoacetate and sodium thiosulphate has been studied at different ionic strengths and 296.16 K. The association constants of the ion-pair, NaIOAc have been calculated using Fuoss-Hsia equation with Fernandez-Prini coefficients from the conductance data and found to be 3.66 and 9.04 dm³ mol⁻¹ at 296.16 and 308.16 K respectively. The rate constants at zero ionic strength for the reaction due to free ions and ion-pairs have been separated from the observed rate constants at different ionic strengths and found to be 0.334 and 9.93 dm³ mol⁻¹ min⁻¹ respectively at 296.16 K. The extent of participation of ion-pairs in the reaction increased with ionic strength of the solution and found to be 12.1% over the ionic strength range (0.004—0.025) studied.

Srivastava¹ reported the kinetics of reaction between sodium iodoacetate and sodium thiosulphate in different aquo-organic solvents at 20°. However, this data was not analysed to find the extent of participation of ion-pairs in the above reaction. The association constants of sodium iodoacetate in water were also not reported earlier. In our previous communication² we have studied the effect of ion-pairs on the kinetics of reaction between potassium peroxysulphate and potassium iodide and showed that iodide ion is oxidized not only by S₂O₇⁻ but also by the ion pair K₂S₂O₅ simultaneously. In continuation of this work we have carried out a detailed investigation of the kinetics of iodoacetate-thiosulphate reaction at different ionic strengths to find out whether ion-pairs participate in this reaction and if so to what extent. Also the conductances of the solutions of sodium iodoacetate in water were measured to find the association constants required for the analysis of the kinetic data.

Materials and Methods
Sodium iodoacetate (Fluka) was used after repeated crystallizations from ethanol and dried in vacuo over P₂O₅. Sodium thiosulphate was of BDH (AR) grade and used as such. The water used was triply distilled and had a specific conductance less than 5 x 10⁻⁷ Scm⁻¹. Equimolar concentrations of sodium iodoacetate and sodium thiosulphate were taken for each kinetic set and the ionic strength varied by varying the concentrations of the reactants themselves. The reaction was followed at 296.16 K by estimating the unreacted thiosulphate with standardized iodine solution using starch as indicator. The experimental details of measuring the conductance was the same as reported earlier³. All the conductance values were corrected for solvent conductance. The overall accuracy of the measured conductance was within ± 0.05%.

Results
The observed molar conductances of sodium iodoacetate in water at 296.16 K and 308.16 K are presented in Table 1. The dielectric constants and viscosities were taken from literature⁴.

The conductance data was first analysed using Shedlovsky extrapolation technique⁵ according to which

\[ \frac{1}{\Delta S(Z)} = \frac{1}{\Delta_0} + (K_A/\Delta_0) c\Delta_0^{1/2} Z \]  

where \( K_A \) is the association constant and other symbols have their usual significance. The activity coefficient \( y_\pm \) was calculated using the Debye - Hückel limiting law equation⁶

\[ \log y_\pm = -A(\alpha c)^{1/2} \]  

<p>| TABLE 1: Molar Conductance of Sodium Iodoacetate in Water at 298.16 and 306.16 K. |
|-----------------------------|-----------------------------|</p>
<table>
<thead>
<tr>
<th>c x 10⁻⁴ mol dm⁻³</th>
<th>( \Lambda / ) Scm mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>296.16K</td>
<td>306.16K</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>50.149</td>
<td>82.250</td>
</tr>
<tr>
<td>37.612</td>
<td>83.091</td>
</tr>
<tr>
<td>30.089</td>
<td>83.749</td>
</tr>
<tr>
<td>25.075</td>
<td>84.653</td>
</tr>
<tr>
<td>21.492</td>
<td>84.933</td>
</tr>
<tr>
<td>18.806</td>
<td>84.933</td>
</tr>
<tr>
<td>16.716</td>
<td>85.016</td>
</tr>
<tr>
<td>15.045</td>
<td>85.243</td>
</tr>
<tr>
<td>12.537</td>
<td>85.527</td>
</tr>
<tr>
<td>10.030</td>
<td>85.946</td>
</tr>
<tr>
<td>8.3582</td>
<td>86.226</td>
</tr>
<tr>
<td>7.1642</td>
<td>86.432</td>
</tr>
<tr>
<td>6.2686</td>
<td>86.491</td>
</tr>
<tr>
<td>5.0149</td>
<td>86.877</td>
</tr>
</tbody>
</table>

\[ D = 78.303 \]  

and \( \eta = 0.008903 \) poise at 296.16 K; and 74.83 and 0.07194 poise at 306.16 K respectively.

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where \( A = 1.8246 \times 10^4 / (\text{DT})^{1/2} \) (\( \text{D} \) is the dielectric constant of the solvent at absolute temperature \( T \)). The degree of dissociation, \( \alpha \), is related to \( S(Z) \) by Eq. (3).

\[
\alpha = 1 - \frac{\Delta S(Z)}{\Delta_a} = \frac{d\log Z}{d\log [\text{reactant}]} = \frac{\Delta S(Z)}{\Delta_a}.
\]  

(3)

Starting from an approximate initial value of \( \Delta_a \), the values \( Z, S(Z), \alpha \) and \( y_{\pm} \) were calculated with the help of a computer in order to find the least square regression values of the slope \( (K_a/\Delta_a)^{1/2} \) and intercept \( (1/\Delta_a) \) according to Eq. 1. The slope and intercept values were then used to evaluate \( \Delta_a \) and \( K_a \). The above procedure was repeated using the fresh intercept values were then used to evaluate \( \Delta_a \) and \( K_a \). The above procedure was repeated using the fresh intercept values were then used to evaluate \( \Delta_a \) and \( K_a \).

The degree of dissociation, \( \alpha \), is related to \( S(Z) \) by Eq. (3). The conductance data was then analysed using the Fuoss-Hsia equation\(^7\) with Fernandez-Prini coefficients\(^7\). This equation is written as

\[
\Delta = \Delta_a - S(ac)c^{1/2} + E \alpha \ln(ac) + J_a ac - J_d(ac)c^{1/2} - K_a \Delta_a c^{-1/2} \alpha c.
\]  

(4)

where the various symbols have their usual significance. The activity coefficients \( (y_{\pm}) \) were calculated from the equation\(^6\)

\[
\log y_{\pm} = A (\alpha c^{1/2} / \{1 + Ba (\alpha c^{1/2} \}) \ldots (5)
\]

Starting with the initial values of \( \Delta_a \) and \( K_a \) obtained from Shedlovsky method and equating the ion-size parameter \( (a) \) to the Bjerrum critical distance \( (q) \) the improved values of \( \Delta_a \) and \( K_a \) were calculated using the least square fitting procedure\(^8\). The standard deviation \( (\sigma) \) was calculated from the relation

\[
\sigma = \sqrt{\sum(\Delta_{\text{exp}} - \Delta_{\text{calc}})^2 / (N-3)}^{1/2} \ldots (6)
\]

where \( N \) is the number of experimental points. These calculations were carried out on a TDC-12 computer and the results are summarized in Table 2.

**Discussion**

From the study of the reaction between \( \text{IOAc}^- \) and \( S_2O_5^2- \) Srivastava\(^4\) concluded that it is a second order reaction being first order with respect to each reactant and an \( S_0^4 \) mechanism has been suggested.

**Table 2 — Association Parameters of Sodium Iodoacetate in Water Using the Fuoss-Hsia Equation**

<table>
<thead>
<tr>
<th>T/K</th>
<th>( q(A') ) (S cm(^{-1}) mol(^{-1}))</th>
<th>( d(q) ) (S cm(^{-1}) mol(^{-1}))</th>
<th>( d(q)/q ) (S cm(^{-1}) mol(^{-1}))</th>
<th>( \Delta )</th>
<th>( K_a )</th>
<th>( S(10^4) )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298.16</td>
<td>3.578</td>
<td>88.703</td>
<td>3.662</td>
<td>0.053</td>
<td>38.60</td>
<td>88.669</td>
<td>2.990</td>
</tr>
<tr>
<td>308.16</td>
<td>3.613</td>
<td>109.52</td>
<td>9.045</td>
<td>0.131</td>
<td>47.98</td>
<td>109.44</td>
<td>7.850</td>
</tr>
</tbody>
</table>

Values obtained from Shedlovsky method are given in parentheses.

![Fig. 1 - Plot of log \( k_{\text{obs}} \) versus \( I^{1/2} \) (curves A and B at low and high ionic strengths respectively) and the plot of \( [\text{NaIOAc}]^2 / [\text{S}_2\text{O}_5\text{OAc}^-]^{1/2} \) versus \( I \) (curve C)](image)

**Fig. 1 - Plot of log \( k_{\text{obs}} \) versus \( I^{1/2} \) (curves A and B at low and high ionic strengths respectively) and the plot of \( [\text{NaIOAc}]^2 / [\text{S}_2\text{O}_5\text{OAc}^-]^{1/2} \) versus \( I \) (curve C)**

The rate law was also given as

\[ -d [S_2O_5^-] / dt = k_{\text{obs}} [\text{IOAc}^-]_{\text{total}} [S_2O_5^-]_{\text{total}} \ldots (7) \]

According to Bronsted-Bjerrum equation\(^9\) for aqueous systems at 25\(^\circ\)

\[ \log k = \log k_0 + 1.018 Z_A Z_B I^{1/2} \ldots (8) \]

Here \( Z_A \) and \( Z_B \) are the charges of the reactants. The slope of the plot of log \( k_{\text{obs}} \) vs. \( I^{1/2} \) should be 2.036 for the above reaction. In the present work at low ionic strengths, i.e. \( I = 0.01 \) the slope was found to be 2.04 (Fig. 1A) in accordance with the theoretical value. However, as the ionic strength increased the experimental points deviated from the theoretical line (Fig. 1B). This could be due to the participation of ion-pairs. Hence the rate law for the reaction may be written as

\[ -d [S_2O_5^-] / dt = k_0^f [\text{IOAc}^-] [S_2O_5^-] \rho_1 \rho_2 / \rho_3 + k_0^p [\text{IOAc}^-] [\text{Na}_2\text{S}_2O_5^-] \rho_2 / \rho_3 + k_0^c [\text{Na}_2\text{OAc}^-] [\text{S}_2O_5^-] + k_0^t [\text{NaIOAc}] [\text{Na}_2S_2] \ldots (9) \]

where \( \rho_1, \rho_2 \) and \( \rho_3 \) are the activity coefficients of the uni-, bi-, and trivalent species present in the solution. The fourth term in Eq. 9 was neglected as the concentrations of the ion-pairs are low (association constants being small) and the product \[\text{NaIOAc} [\text{Na}_2S_2] \]
O₃] would be very small. By incorporating the association constants

\[ K_1 = [\text{NaIOAc}]/[\text{Na}^+] [\text{IOAc}^-] \] (10) \]

\[ K_2 = [\text{Na}_{2}S_{2}O_{5}^-]/[\text{Na}^+] [S_{2}O_{5}^{2-}] \] \]

Eq. (9) can be rewritten as

\[ -d[S_{2}O_{5}^{2-}] / dt = [\text{IOAc}^-] [S_{2}O_{5}^{2-} \{K_{f} y_{1} y_{2} + [\text{Na}^+] (K_{g} k_{p} + K_{l} k_{p}^{2})\} \]

or

\[ -d[S_{2}O_{5}^{2-}] / dt = k_{obs} (1 + [\text{Na}^+] K_{y_{2}}) (1 + [\text{Na}^+] K_{y_{2}}) [\text{IOAc}^-] [S_{2}O_{5}^{2-}] \] \]

where \( k_{p} \) is the rate constant for free ions and \( k_{p} \) that of ion-pairs at zero ionic strength. The first term of Eq. (13) refers to the simple reaction between IOAc and \( S_{2}O_{5}^{2-} \) ions and second term to the reactions due to ion-pair \( (k_{p} = k_{p} + K_{l} k_{p}^{2}) \). Since the \( [\text{IOAc}]_{\text{total}} \) and \( [S_{2}O_{5}^{2-}]_{\text{total}} \) are equal to \((1 + [\text{Na}^+] K_{y_{1}} y_{1}^{2}) [\text{IOAc}^-] \) and \((1 + [\text{Na}^+] K_{y_{2}} y_{2}^{2}) [S_{2}O_{5}^{2-}] \) respectively. Eq. (7) can be written as

\[ -d[S_{2}O_{5}^{2-}] / dt = k_{obs} (1 + [\text{Na}^+] K_{y_{2}}) (1 + [\text{Na}^+] K_{y_{2}}) [\text{IOAc}^-] [S_{2}O_{5}^{2-}] \]

Equating (13) and (14) and rearranging we get

\[ k_{obs} (1 + [\text{Na}^+] K_{y_{2}}) (1 + [\text{Na}^+] K_{y_{2}}) y_{1} y_{2} y_{2} = k_{p} + k_{p} [\text{Na}^+] y_{1} y_{2} y_{2} \]

The concentrations of free ions \( \text{Na}^+, S_{2}O_{5}^{2-}, \text{IOAc}^- \) and activity coefficients \( y_{1}, y_{2} \) and \( y_{3} \) were calculated as follows.

If \( m \) is the molar concentration of the reactants, \( \alpha \) and \( \beta \) are the degree of dissociation of the ion-pair \( \text{NaIOAc} \) and \( \text{Na}_{2}S_{2}O_{5}^- \) respectively, then the concentrations of \( \text{Na}^+ \) \( \text{IOAc}^- \), \( \text{Na}_{2}S_{2}O_{5}^- \) and \( \text{Na}

\[ S_{2}O_{5}^{2-} \] are \((1 + \alpha + \beta) m, \alpha m, (1 - \alpha) m, \beta m \) and \((1 - \beta) m \) respectively. The ionic strength of the system and the thermodynamic association constants \( K_1 \) and \( K_2 \) are given by Eqs (16-18).

\[ \log y_{1} = AZ_{1} (1/2)/1 + 1/2 - 0.3 I \]

Here \( y_{1}, y_{2} \) and \( y_{3} \) were assumed to be unity in Eq. (17) and taking \( K_{1} \) as 3.662 dm\(^{3}\)mol\(^{-1}\) (obtained from conductance measurements in the present work, Table 2) the value of \( \alpha \) was calculated. This \( \alpha \) was then substituted in Eq. (18) to get the improved value of \( \beta \). For this the value of \( K_{2} \) was taken as 3.846 dm\(^{3}\)mol\(^{-1}\) from the work of Monk and Gimblett. These \( \alpha \) and \( \beta \) values were then substituted in Eq. (16) to get an improved value of \( I \). This procedure was repeated several times till constant values for \( \alpha, \beta \) and \( I \) were obtained.

The values of \( k_{obs} \) and \( \text{Na}^+ \) are given in Table 3. According to Eq. (15) the plot of \( k_{obs} \) and \( [\text{Na}^+] \) \( K_{y_{1}} y_{1}^{2} \) \( (1 + [\text{Na}^+] K_{y_{2}} y_{2}^{2}) \) versus \( [\text{Na}^+] \) \( K_{y_{2}} y_{2}^{2} \) should be linear with an intercept \( k_{p} \) and slope \( k_{p} \).

The values of \( k_{obs} \) and \( [\text{Na}^+] \) were obtained (Fig 2A) in the present work and from the intercept and slope values \( k_{p} \) and \( k_{p}^{2} \) were found to be 0.334 and 9.93 dm\(^{3}\)mol\(^{-1}\) min\(^{-1}\) respectively. We have also analysed some of the kinetic data obtained by Srivastava and the results are tabulated in Table 3. The required value of \( K_{1} \) at 20° for the analysis of this data was extrapolated from the association constant data reported in the present work and \( K_{2} \) at 20° obtained from the data of Monk and Gimblett. The \( k_{p} \) and \( k_{p}^{2} \) were found to be 0.285 and 3.91 dm\(^{3}\)mol\(^{-1}\) min\(^{-1}\) from the data reported by Srivastava at 20°.

An alternative analysis of the kinetic data was also made for the sake of comparison on the lines of Table 3 — RATE CONSTANTS, [Na\(^{+}\)], [Na\(_{2}\)S\(_{2}\)O\(_{5}\)\(^{-}\)], [NaI0Ac] AT VARIOUS CONCENTRATIONS OF REACTANTS FOR Na\(_{2}\)S\(_{2}\)O\(_{5}\) AND NaIOAc REACTION AT 296.16K.

<table>
<thead>
<tr>
<th>( m ) (mol dm(^{-3}))</th>
<th>( k_{obs} ) (dm(^{3}) mol min(^{-1}))</th>
<th>( [\text{Na}^{+}] ) (mol dm(^{-3}))</th>
<th>( [\text{Na}<em>{2}\text{S}</em>{2}\text{O}_{5}^{-}] \times 10^{6} ) (mol dm(^{-3}))</th>
<th>( [\text{NaIOAc}] \times 10^{6} ) (mol dm(^{-3}))</th>
<th>( I )</th>
<th>( (I) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0010</td>
<td>0.454</td>
<td>0.002982</td>
<td>0.00866</td>
<td>0.00944</td>
<td>0.003973</td>
<td>0.05810</td>
</tr>
<tr>
<td>0.0015</td>
<td>0.487</td>
<td>0.004461</td>
<td>0.01833</td>
<td>0.02054</td>
<td>0.005943</td>
<td>0.06979</td>
</tr>
<tr>
<td>0.0020</td>
<td>0.520</td>
<td>0.005934</td>
<td>0.03098</td>
<td>0.03546</td>
<td>0.007903</td>
<td>0.07927</td>
</tr>
<tr>
<td>0.0025</td>
<td>0.540</td>
<td>0.007400</td>
<td>0.04638</td>
<td>0.05403</td>
<td>0.009853</td>
<td>0.08734</td>
</tr>
<tr>
<td>0.0030</td>
<td>0.563</td>
<td>0.008860</td>
<td>0.06426</td>
<td>0.07065</td>
<td>0.01795</td>
<td>0.09443</td>
</tr>
<tr>
<td>0.0035</td>
<td>0.583</td>
<td>0.010314</td>
<td>0.08449</td>
<td>0.10140</td>
<td>0.013730</td>
<td>0.10077</td>
</tr>
<tr>
<td>0.0040</td>
<td>0.605</td>
<td>0.011763</td>
<td>0.10692</td>
<td>0.12992</td>
<td>0.015656</td>
<td>0.10651</td>
</tr>
<tr>
<td>0.0045</td>
<td>0.622</td>
<td>0.013207</td>
<td>0.13140</td>
<td>0.16151</td>
<td>0.017576</td>
<td>0.11178</td>
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<tr>
<td>0.0050</td>
<td>0.640</td>
<td>0.014646</td>
<td>0.15755</td>
<td>0.19605</td>
<td>0.019488</td>
<td>0.11665</td>
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<tr>
<td>0.00625</td>
<td>0.680</td>
<td>0.018223</td>
<td>0.23206</td>
<td>0.29486</td>
<td>0.024241</td>
<td>0.12745</td>
</tr>
</tbody>
</table>

**Srivastava Data at 20°**: \( K_{1} = 2.481 \) & \( K_{2} = 3.704 \) dm\(^{3}\)mol\(^{-1}\)
were obtained. Then the I. h. s. of Eq. (20) was plotted against f(I) (Fig. 1C) and from the intercept \( k_{ip} \) was obtained to be 9.85 dm\(^3\) mol\(^{-1}\) min\(^{-1}\) in good agreement with the value of 9.93 dm\(^3\) mol\(^{-1}\) min\(^{-1}\) obtained by the previous analysis.

The percentage contributions of ion-pairs reaction to the overall reaction was calculated from Eq. (22)

\[
\% \text{contribution of the ion-pair reaction} = 100 \left( \frac{v - v_i}{v} \right)
\]

The values so calculated were found to be 12.1 at 25\(^\circ\) and 4.63 at 20\(^\circ\). This could be due to the ion-association being more at higher temperatures. This receives support from the data in Table 2 (\(K_4\) values are higher at 25\(^\circ\) than those at 20\(^\circ\)).

References