Mn$^{II}$ catalysed Periodate Oxidation of anilines – Thermodynamic and Isokinetic studies

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Abstract: This paper reports the studies made on the reaction series, Mn$^{II}$ catalysed periodate oxidation of aromatic amines in acetone-water medium. Twenty aromatic amines were subjected to oxidation by periodate in presence of Mn$^{II}$ catalyst. The progress of reactions was followed spectrophotometrically by recording the absorbance of the reaction mixture at pre-determined absorption maxima of the reaction intermediate at different time. From the rate constants determined at four different temperatures, the values of thermodynamic parameters, viz., activation energy (ΔE), entropy of activation (ΔS$^*$), Arrhenius frequency factor (A), free energy of activation (ΔG$^*$) and enthalpy of activation (ΔH$^*$) were determined using Arrhenius equation and other well known equations. The reactions of series are characterized by small value of activation energy and large negative value of entropy of activation. The value of ΔG$^*$ was temperature dependent. A high negative value of ΔS$^*$ is suggestive of solvent interactions with the reactive species and of the probability that the transition state may be solvated. Small value of activation energy is characteristic of catalysed reaction. The reaction series under consideration, follows the isokinetic relationship suggesting that the same interaction mechanism may be followed in the oxidation of these substituted anilines. The isokinetic temperature as evaluated from the slope of the isokinetic line is 273.5 K.

Key Words: Thermodynamic parameters, Isokinetic relationship, Mn$^{II}$ catalysed, Periodate, Anilines.

Introduction

Most of the aromatic amines are enlisted as toxic and/or carcinogenic chemicals by Toxic Release inventory, US EPA, Pollution inventory, UK, and International Agency for Research on cancer. Aromatic amines have been subjected to oxidation reactions by using oxidants like benzimidazolium fluorochromate, peroxydisulphate ion and periodate. A detailed survey of literature on periodate oxidation of organic compounds reveals that much work on periodate oxidation of various classes of organic compounds has been carried out from synthesis point of view and a large amount of work on the kinetics of oxidation of 1, 2-diols and related compounds (Malapradian oxidation) has been reported and fairly satisfactory picture of mechanism of these processes is available. There are two reviews by Sklarz and Dryhurst available on periodate oxidation of organic compounds. However, comparatively lesser work on the mechanistic aspect of non-Malapradian oxidations of organic compounds, including the oxidation of aromatic amines, has been carried out. Tanabe, in a series of papers, studied the products of periodate oxidation of aniline at different pH and found that the products are different at different pH. As regards the studies on kinetics of uncatalysed periodate oxidation of other aromatic amines, there are only a few reports available. Recent reports have been made by Kaushik et al. and include the Mn$^{II}$ catalyzed periodate oxidation of 2,3-xylidine, 2,4-xylidine, 2,6-xylidine, N-methylaniline, N,N-diethyl-m-toluidine, p-toluidine and 4-chloro-2-methylaniline. These
reactions have been studied under different pH conditions and the thermodynamic parameters have been reported on the basis of kinetic studies. Salvation effects have been taken into account while proposing mechanism for these reactions. Exhaustive survey of literature indicates that there are no other reports available for Mn\(^{II}\) catalysed periodate oxidation of aromatic amines. Present communication presents the thermodynamic studies made on the Mn\(^{II}\) catalysed periodate oxidation of twenty substituted anilines with an aim to evaluate the thermodynamic parameters and to test the isokinetic relationship for the reactions of this series to ascertain whether all reactions of the series follow similar mechanism. As the reactions are sensitive to the pH and dielectric constant of the medium, the studies have been made under similar conditions. The studies are important for their further expected use in developing methods for detection and treatment of anilines as well as for developing a general understanding about them.

**Experimental**

**Materials:**

All chemicals used were of Aldrich/E. Merck analytical reagent/guaranteed reagent grade and used after redistillation/recrystallization. Triply distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer\(^{26}\), consisting of different volumes of 0.05 M oxalic acid, 0.02 M boric acid, 0.05 M succinic acid, 0.05 M sodium sulphate and 0.05 M borax, was used for maintaining the pH.

**Kinetic procedure:**

As the aim of the present investigation was to study the validity of isokinetic relationship for this reaction series, all reactions were studied in similar conditions of pH, dielectric constant etc. as shown in Table 2. For studying the kinetics, the reactions were studied in a spectrophotometric cell and initiated by adding temperature equilibrated NaIO\(_4\) solution of known concentration to the reaction mixture containing the aniline, Mn\(^{II}\) and buffer and maintained at the desired temperature (± 0.1\(^\circ\)C). Desired temperature was maintained with the help of a high precision thermostatic control. The progress of the reaction was followed by recording the absorbance on Shimadzu double beam spectrophotometer (UV Pharmaspec-2450), at the absorption maxima of the reaction mixture(\(\lambda_{\text{max}}\)). \(\lambda_{\text{max}}\) was not found to change with time under experimental conditions. Table 2 gives the absorption maxima of the reaction mixtures in case of different reactions studied by us. Fig. 1 gives rapid UV-VIS scans of reaction solution at different time for one of the reactions studied. The reactions of the series were studied under pseudo first order conditions by taking oxidant in excess.

**Evaluation of pseudo first order rate constant:**

As the \(k_{\text{obs}}\) (first order rate constant) values are essential to calculate the various thermodynamic parameters, the Guggenhein method\(^{27}\) was applied to find out the \(k_{\text{obs}}\) values. Accordingly, a series of absorbance readings (equivalent to concentration of the intermediate being formed in the reactions), ‘\(A_0\)’, is recorded at times \(t\) with equal intervals. A second series of readings \(A_{t+\Delta t}\) is also made, each at time \(t+\Delta t\), where \(\Delta t\) is arbitrary but constant interval of time chosen. A plot of log (\(A_{t+\Delta t}-A_t\)) vs \(t\) should give a straight line, with slope equal to \(-k_0/2.303\). Hence \(k_{\text{obs}}\), the first order rate constant, can be calculated from the slope. Before applying this method, it is necessary to ascertain by independent method that the reaction conforms to the first order behaviour.

**Evaluation of overall rate constant:**

The reactions of the series were found to be first order in substrate, Mn\(^{II}\) and periodate each. The pseudo first order rate constants (\(k_{\text{obs}}\)) were divided by [S] and Mn\(^{II}\) to get the overall rate constant (\(k_{\text{cat}}\)). Here [S] is the concentration of the reactant taken in excess. As already mentioned, periodate was taken in excess.

**Evaluation of thermodynamic Parameters:**

A plot of log \(k_{\text{cat}}\) vs 1/T was drawn to get the Arrhenius plot relating the temperature and specific rate, viz:

\[
\log k_{\text{cat}} = [-\Delta E / 2.303 RT] + \text{Constant}
\]  

(1)

The energy of activation was then calculated from the slope of this curve as well as by the application of the equation:
The frequency factor \((A)\), free energy of activation \((\Delta F^\#)\), enthalpy of activation \((\Delta H^\#)\) and entropy of activation \((\Delta S^\#)\) were determined by the application of following relationships,

\[
k_{cat} = A \cdot e^{-\Delta E/RT} \quad (3)
\]
\[
k_{cat} = [kT/h] \cdot e^{-\Delta G^#/RT} \quad (4)
\]
\[
k_{cat} = [kT/h] \cdot e^{-\Delta E/RT} \cdot e^{\Delta S^#/R} \quad (5)
\]

and

\[
\Delta H^\# = \Delta G^# + T \Delta S^\# \quad (6)
\]

which are valid for reactions in solution\(^{27}\). In the above equation \(k\) stands for Boltzman constant, \(h\) is Planck’s constant, \(e\) is a constant having a value 2.718, and other symbols have their usual meaning.

**Stoichiometry and Product Analysis:**

For different reactions of this series, the faster colour changes in the reaction mixtures relative to the separation of product on standing for long time indicates the formation of the colored intermediate on a time scale of minutes and that of the final product on a time scale of hours. The overall reaction appears to involve several steps and possibly several transient intermediates.

Stoichiometry of the reaction was determined by allowing a known excess of NaIO\(_4\) to react with substrate. After completion of the reaction, the precipitated product was filtered out and in the filtrate unconsumed NaIO\(_4\) was determined iodimetrically. The curve obtained in graphical plot between \(\log (a-x)\) versus time (where \(a-x\) is the concentration of unreacted periodate) followed the pseudo first order behaviour upto a point after which the inflexion was obtained. It was taken as the point corresponding to the completion of first stage of reaction for which the kinetic studies were made. The results indicated the stoichiometry to be 1 mol of aniline: 2 moles periodate for the initial part of the reaction. Fig. 2 shows the break in stoichiometry curves indicating the first stage in one of the reactions. As an example the reaction in case of oxidation of a xylidine\(^{18-20}\) can be written as follows:

\[
\text{Mn}^{II} \quad \text{CH}_3\text{CH}_3\text{C}_6\text{H}_3\text{NH}_2 + 2\text{IO}_4^- + 2\text{H}^+ \quad \text{CH}_3\text{CH}_3\text{C}_6\text{H}_2\text{O}_2 + 2\text{HIO}_3 + \text{NH}_3 \quad (7)
\]

Reaction mixtures containing oxidant in excess were left overnight for completion of the reaction and filtered. The filtrate was extracted with petroleum ether (40–60°C). The extract was evaporated at room temperature and subjected to separation using TLC. The remaining part of the filtrate might be containing other products of this reaction that could not be separated and identified. The separated compounds were recrystallized in petroleum ether and characterized on the basis of test for quinone, melting point and spectral studies\(^{12-25}\). The details of the characterization studies are not being discussed in this paper. The main reaction products for the reactions of the series are given in Table-1.

**Results**

**Preliminary observations:**

On mixing the reactants, the solution becomes coloured which later changes in to another colour. On keeping for long time, it finally gives the product. These observations indicate the formation of more than one intermediate prior to the formation of final reaction product. The absorption maxima of the reaction mixtures are in visible region, while the UV-VIS spectra of IO\(_4^-\), substrate and Mn\(^{II}\) indicated these to show no absorption in visible region. Hence, for following the kinetics the absorbance changes were recorded at absorption of reaction mixture at which only the reaction intermediate absorbed.

**Rate Law:**

In addition to the reports on some of the reactions of the series\(^{18-25}\), all other reactions of this series were also found to be first order in each of substrate, oxidant and the catalyst. The kinetics was studied under pseudo order conditions by keeping generally the periodate concentration in excess. For evaluation of Plane mirror
method was used for evaluation of initial rates. Guggenheim’s method was used for evaluation of pseudo first order rate constants, $k_{\text{obs}}$. Under these conditions, the kinetics was defined by the rate law (2).

$$\frac{d[C]}{dt} = k_{\text{cat}} [\text{DMA}]_0 [\text{IO}_4^-]_0 [\text{Mn}^{\text{II}}] = k_{\text{obs}} [\text{DMA}]_0$$

(8)

where, $[\text{DMA}]_0 = \text{initial concentration of the substrate amine}$, $[\text{IO}_4^-]_0 = \text{initial concentration of periodate(taken in excess)}$, $k_{\text{obs}} = k_{\text{cat}} [\text{IO}_4^-]_0 [\text{Mn}^{\text{II}}]$, and $k_{\text{cat}} = \text{rate constant for Mn}^{\text{II}} \text{catalysed pathway}$. In the absence of Mn$^{\text{II}}$, no significant reaction occurred. The values of $k_{\text{cat}}$ obtained at different [Mn$^{\text{II}}$], [IO$_4^-$]$_0$ and [DMA]$_0$ are seen to be in good agreement and consistent with the rate law (2). This trend has been found in all reactions studied. Further, rate-pH profile shows a maximum in case of every reaction studied.

**Thermodynamic Parameters:**

From the rate constants determined at four different temperatures, the values of thermodynamic parameters were determined and the mean values are given in Table-2.

**Isokinetic Relationship:**

In case of oxidation of various substituted anilines by periodate ion in acetone-water medium, the $\Delta S^\#$ values were plotted against the corresponding $\Delta H^\#$ values in order to see whether the oxidation of different anilines in acetone-water medium follows the isokinetic relationship. The plot is shown in Fig. 3 and the values of $\Delta S^\#$ and $\Delta H^\#$ are summarized in Table 2.

**Table-1: Absorption Maxima for reaction mixtures and Main Reaction products of different reactions of the series- Mn$^{\text{II}}$ catalysed periodate oxidation of anilines**

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Aromatic amine oxidized</th>
<th>Main Reaction Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aniline</td>
<td>2,5-dianilino-p-benzoquinoneimine</td>
</tr>
<tr>
<td>2</td>
<td>p-bromoaniline</td>
<td>4-bromo-1,2-benzoquinone</td>
</tr>
<tr>
<td>3</td>
<td>p-phenetidine</td>
<td>4-ethoxy-1,2-benzoquinone</td>
</tr>
<tr>
<td>4</td>
<td>p-anisidine</td>
<td>4-methoxy-1,2-benzoquinone</td>
</tr>
<tr>
<td>5</td>
<td>m-toluidine</td>
<td>4-methyl-1,4-benzoquinone</td>
</tr>
<tr>
<td>6</td>
<td>2,3-xylidine</td>
<td>2,3-dimethyl-1,4-benzoquinone</td>
</tr>
<tr>
<td>7</td>
<td>p-chloroaniline</td>
<td>4-chloro-1,2-benzoquinone</td>
</tr>
<tr>
<td>8</td>
<td>p-toluidine</td>
<td>4-methyl-1,2-benzoquinone</td>
</tr>
<tr>
<td>9</td>
<td>4-chloro, 2-methylaniline</td>
<td>5-chloro,3-methyl-1,2-benzoquinone</td>
</tr>
<tr>
<td>10</td>
<td>m-anisidine</td>
<td>4-methoxy-1,2-benzoquinone</td>
</tr>
<tr>
<td>11</td>
<td>m-chloroaniline</td>
<td>4-chloro-1,2-benzoquinone</td>
</tr>
<tr>
<td>12</td>
<td>p-ethylaniline</td>
<td>4-ethyl-1,2-benzoquinone</td>
</tr>
<tr>
<td>13</td>
<td>o-anisidine</td>
<td>Methoxy-1,4-benzoquinone</td>
</tr>
<tr>
<td>14</td>
<td>o-chloroaniline</td>
<td>Chloro-1,4-benzoquinone</td>
</tr>
<tr>
<td>15</td>
<td>5-chloro, 2-methylaniline</td>
<td>2-chloro,5-methyl-1,4-benzoquinone</td>
</tr>
<tr>
<td>16</td>
<td>2,5-xylidine</td>
<td>2,5-dimethyl-1,4-benzoquinone</td>
</tr>
<tr>
<td>17</td>
<td>o-toluidine</td>
<td>Methyl-1,4-benzoquinone</td>
</tr>
<tr>
<td>18</td>
<td>N,N-dimethylaniline</td>
<td>Tautomeric mixture of O-methylquinoneoxime and p-nitrosoanisole</td>
</tr>
<tr>
<td>19</td>
<td>N-methylaniline</td>
<td>p-benzoquinone</td>
</tr>
<tr>
<td>20</td>
<td>N- ethylaniline</td>
<td>p-benzoquinone</td>
</tr>
</tbody>
</table>
Table-2: Thermodynamic Parameters for different reactions of the series
pH = 4.5, [Mn] = 1.456 × 10^{-7} mol dm^{-3}, acetone = 10%

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Substituent</th>
<th>λ_{max} (nm)</th>
<th>Temp. Coefficient</th>
<th>ΔE kJ mol^{-1}</th>
<th>A dm^{3} mol^{-1} s^{-1}</th>
<th>-ΔS^\circ J mol^{-1} K^{-1}</th>
<th>ΔH^\circ kJ mol^{-1}</th>
<th>ΔG^\circ kJ mol^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>360</td>
<td>1.25</td>
<td>18.13</td>
<td>3.60 × 10^{9}</td>
<td>162.33</td>
<td>15.51</td>
<td>66.72</td>
</tr>
<tr>
<td>2</td>
<td>p-Br</td>
<td>452</td>
<td>1.34</td>
<td>23.95</td>
<td>3.40×10^{10}</td>
<td>143.84</td>
<td>21.33</td>
<td>66.71</td>
</tr>
<tr>
<td>3</td>
<td>p-OC_{2}H_{5}</td>
<td>495</td>
<td>1.54</td>
<td>35.88</td>
<td>4.80 × 10^{13}</td>
<td>101.08</td>
<td>33.26</td>
<td>65.15</td>
</tr>
<tr>
<td>4</td>
<td>p-CH_{3}</td>
<td>475</td>
<td>1.67</td>
<td>42.05</td>
<td>4.98×10^{14}</td>
<td>81.54</td>
<td>39.43</td>
<td>65.16</td>
</tr>
<tr>
<td>5</td>
<td>m-CH_{3}</td>
<td>545</td>
<td>1.24</td>
<td>17.55</td>
<td>4.00 × 10^{9}</td>
<td>163.56</td>
<td>14.93</td>
<td>66.53</td>
</tr>
<tr>
<td>6</td>
<td>2,3-DMA</td>
<td>469</td>
<td>1.25</td>
<td>17.57</td>
<td>1.24 × 10^{9}</td>
<td>165.65</td>
<td>14.94</td>
<td>67.21</td>
</tr>
<tr>
<td>7</td>
<td>p-Cl</td>
<td>475</td>
<td>1.16</td>
<td>12.30</td>
<td>1.93×10^{8}</td>
<td>182.16</td>
<td>9.67</td>
<td>67.13</td>
</tr>
<tr>
<td>8</td>
<td>p-CH_{3}</td>
<td>474</td>
<td>1.58</td>
<td>38.07</td>
<td>3.30×10^{13}</td>
<td>96.35</td>
<td>35.44</td>
<td>65.84</td>
</tr>
<tr>
<td>9</td>
<td>4,2-CMA</td>
<td>490</td>
<td>1.48</td>
<td>33.15</td>
<td>1.77×10^{12}</td>
<td>113.84</td>
<td>30.53</td>
<td>66.45</td>
</tr>
<tr>
<td>10</td>
<td>m-OCH_{3}</td>
<td>472</td>
<td>1.35</td>
<td>24.52</td>
<td>4.74×10^{10}</td>
<td>141.81</td>
<td>21.90</td>
<td>66.64</td>
</tr>
<tr>
<td>11</td>
<td>m-Cl</td>
<td>370</td>
<td>1.57</td>
<td>35.81</td>
<td>3.56×10^{12}</td>
<td>106.00</td>
<td>33.18</td>
<td>66.63</td>
</tr>
<tr>
<td>12</td>
<td>p-C_{6}H_{5}</td>
<td>470</td>
<td>1.19</td>
<td>14.58</td>
<td>1.86×10^{9}</td>
<td>172.31</td>
<td>11.96</td>
<td>66.32</td>
</tr>
<tr>
<td>13</td>
<td>o-OCH_{3}</td>
<td>470</td>
<td>1.83</td>
<td>48.22</td>
<td>9.07×10^{13}</td>
<td>61.47</td>
<td>45.64</td>
<td>64.66</td>
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<tr>
<td>14</td>
<td>o-Cl</td>
<td>460</td>
<td>1.62</td>
<td>39.29</td>
<td>7.62×10^{12}</td>
<td>95.97</td>
<td>36.67</td>
<td>66.95</td>
</tr>
<tr>
<td>15</td>
<td>5,2-CMA</td>
<td>484</td>
<td>1.58</td>
<td>38.21</td>
<td>9.97×10^{14}</td>
<td>102.36</td>
<td>35.59</td>
<td>67.88</td>
</tr>
<tr>
<td>16</td>
<td>2,5-DMA</td>
<td>472</td>
<td>1.55</td>
<td>37.71</td>
<td>7.80×10^{12}</td>
<td>99.86</td>
<td>35.08</td>
<td>66.59</td>
</tr>
<tr>
<td>17</td>
<td>o-CH_{3}</td>
<td>525</td>
<td>1.27</td>
<td>19.51</td>
<td>4.42×10^{8}</td>
<td>162.71</td>
<td>16.89</td>
<td>68.22</td>
</tr>
<tr>
<td>18</td>
<td>N,N-DMA</td>
<td>474</td>
<td>1.70</td>
<td>43.95</td>
<td>2.05×10^{13}</td>
<td>82.63</td>
<td>41.33</td>
<td>67.40</td>
</tr>
<tr>
<td>19</td>
<td>N-CH_{3}</td>
<td>533</td>
<td>1.31</td>
<td>22.04</td>
<td>5.27×10^{9}</td>
<td>151.95</td>
<td>19.42</td>
<td>67.36</td>
</tr>
<tr>
<td>20</td>
<td>N- C_{6}H_{5}</td>
<td>534</td>
<td>1.80</td>
<td>49.36</td>
<td>2.05×10^{13}</td>
<td>69.24</td>
<td>46.73</td>
<td>68.58</td>
</tr>
</tbody>
</table>

Fig.1 UV-VIS Scan at different time for the Mn^{II} catalysed periodate oxidation of N,N-dimethylaniline at [NaIO_{4}] = 3.0 × 10^{-4} mol dm^{-3}, [N,N-dimethylaniline] = 1.0 × 10^{-5} mol dm^{-3}, [Mn^{II}] = 1.456 × 10^{-7} mol dm^{-3}, Acetone = 10.0 % (v/v), Temp = 30 ± 0.1°C, pH = 4.5
Fig. 2 Determination of Stoichiometry of the reaction of Mn$^{II}$ catalyzed periodate oxidation of $p$-anisidine at $[p$-anisidine] = $1.0 \times 10^{-3}$ mol dm$^{-3}$, $[\text{Mn}^{II}] = 1.456 \times 10^{-7}$ mol dm$^{-3}$, pH = 4.5, acetone = 10.0 % (v/v)

Fig. 3 Isokinetic relationship for Mn$^{II}$ catalyzed periodate oxidation of anilines at pH = 4.5, $[\text{Mn}^{II}] = 1.456 \times 10^{-7}$ mol dm$^{-3}$, acetone = 10.0 %
Discussion

The value of $\Delta G^\#$ was temperature dependent. Statistical analysis confirmed that the standard errors of $\Delta H^\#$ and $\Delta S^\#$ correlate and lead to the centre of temperature range used as discussed in an article by Lente et al.\textsuperscript{28}, as given by the relation, $T_{\text{isok}} = \sigma(\Delta H^\#)/\sigma(\Delta S^\#)$. An examination of the thermodynamic parameters for different anilines would reveal that all of these reactions are characterized by a large negative value of entropy of activation ranging from $-61.47$ to $-182.16$ J mol$^{-1}$ K$^{-1}$. Further, the energy of activation is low in each case. Small value of activation energy is characteristic of catalysed reaction. A high negative value of $\Delta S^\#$ is suggestive of solvent interactions leading to predominant salvation effects and of the probability that the transition state may be solvated. High negative $\Delta S^\#$ values are usually observed for reactions in less polar solvents. Since the reactions under study are expected to be ion-dipole type, it is also expected that the entropy of the activated complex for all the substituted anilines should be nearly the same. However, because of the difference in the polarity of different substituted anilines the extent of solvation should be different and hence, the experimental value of $\Delta S^\#$ differs from aniline to aniline.

For a large number of reaction series, it is found that $\partial \Delta H^\#$ and $\partial \Delta S^\#$ are proportional\textsuperscript{29}. This experimental observation is expressed by equation (1), in which $\beta$ is a constant of proportionality.

$$\partial \Delta H^\# = \beta \times \partial \Delta S^\#$$  \hspace{1cm} (9)

$$\partial \Delta G^\# = \partial \Delta H^\# - T \cdot \partial \Delta S^\#$$  \hspace{1cm} (10)

On combining Eq. (5) with Eq. (6), we get Eq. (7)

$$\partial \Delta G^\# = (1 - T/\beta) \cdot \partial \Delta H^\#$$  \hspace{1cm} (11)

When $\beta = T$, $\partial \Delta F^\# = 0$, and no variation of equilibrium or rate will be expected on changing the substituent and the media. If enthalpies and entropies are insensitive to temperature changes or if the change in temperature is small, $\beta$ will equal to $T$ at a real temperature - one at which all the members of a series will react at the same rate. Normally, these conditions are not met. Therefore, $\beta$ is best considered a mathematical slope rather than a phenomenological temperature\textsuperscript{30}. The value of $\beta$ is called as the isokinetic temperature.

If a single interaction mechanism is involved in producing $\partial \Delta F^\#$, $\partial \Delta H^\#$, or $\partial \Delta S^\#$, equation (7) can be expected to apply. In such cases a plot of $\Delta H^\#$ vs $\Delta S^\#$ should also be linear according to equation (5). In these cases, the isokinetic temperature is an inversion point of relative reactivities or equilibria. The reaction exhibiting the fastest rate or largest equilibrium constant below the isokinetic temperature will be the slowest above it.

At temperature below $\beta$, the reaction rate or equilibrium is controlled mainly by $\partial \Delta H$. In this region the reaction with the lowest activation energy will react fastest and interpretations involving potential energy surfaces can be made. At the temperature above $\beta$, however, the controlling factor is $\partial \Delta S$, and interpretations based upon potential energy surface would obviously be in error. Generalizations concerning the effects of structure or solvent on reactivity or equilibrium can not be valid for two reaction series if the generalizations are made from a study of one reaction series below the isokinetic temperature and applied to a second series studied above the isokinetic temperature. However, conclusions drawn from study of reaction series are normally supported by other type of evidence or, alternatively, the effect of temperature variation can be studied so that the isokinetic temperature is known.

When a structural change in a given part of a molecule fails to affect the reaction rate, two explanations are possible in principle. One is that the reactions have been studied at the isokinetic temperature. The other is that the reaction mechanism does not involve any variable interactions between the reaction site and the part of the molecule in which structural change was made.

Occasionally, differences in the activation energy have been used as evidence for a change in reaction mechanism in the belief that this is a sound procedure even when the use of differences in free energy of activation would not be. This practice can also be misleading. For example, it is not unusual for reactions representing the extremes of a single isokinetic line, and hence very probably having the same reaction mechanisms, to differ in activation energy by 5 K Cal. mol$^{-1}$ or even more\textsuperscript{21}. A reaction of different mechanism will probably be displaced from a isokinetic line and will probably differ considerably in rate constant, but it might easily have the same activation energy at one of the points on the isokinetic line. Some other points on
the isokinetic line will probably have the same entropy as the reaction in question, so that will not do as a criterion of change in mechanism either.

It is seen from the isokinetic plot (Fig. 3) that the points show a good correlation, the correlation coefficient (r) and coefficient of determination (r²) being 0.973 and 0.947 respectively. It suggests that 97.3 % variations in the value of ΔH° are due to the effect of ΔS° and the remaining 2.69 % variation can be attributed to other causes. The intercept of isokinetic line is 16.52 with standard deviation of 0.65. The value of ‘t’ as calculated by employing the significance test at 0.01 significance level, is 11.7. It is well above the tabulated value at this significance level and suggests that there are less than 1.0% chances of involvement of errors in drawing the conclusions. The slope (β) of the isokinetic line, calculated by the method of least squares, is found to be 273.5 K, which is the isokinetic temperature for this reaction. A linear relationship between ΔS° and ΔH° suggests that the same interaction mechanism may be followed in the oxidation of these substituted anilines. However, it may be pointed out that a high correlation coefficient does not always indicate the presence of a single interaction mechanism. A straight line may be obtained even in the presence of two interaction mechanisms, if their β values happen to be equal. In spite of the above uncertainties involved, it is reasonable to assume in this case that the same interaction mechanism is probably being followed as other kinetic features go to support this conclusion. The probable mechanism for the reactions of this series can be visualized by visiting the already published articles on some of the reactions.

References


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