A large number of N-haloimides (or imides) including some N-fluro compounds, have since been prepared and tested as reagents for allylic bromination and oxidation of organic compounds. Only a few of these compounds have been found to have distinct advantages for routine work; others remain of academic interest only. The only reagents which have been found to have as wide acceptability as NBS for allylic bromination are the N-bromohydantoins. However, some of the reagents which were found to be poor allylic brominating reagents have proved to be better reagents in certain other reactions, particularly those involving the use of a polar medium and where the reaction proceeds by an ionic rather than a free radical mechanism. N-chlorosuccinimide and N-bromosuccinimide for example, have proved to be stronger oxidants.

N-bromosuccinimide is a source of positive halogen, and this reagent has been exploited\(^1\) as oxidant for a variety of substrates in both acidic and alkaline medium. The use of N-bromosuccinimide as an oxidant in acidic medium is extensive\(^2\) and it has also been used in the determination of some organic compounds\(^3\). This potent oxidising agent has chiefly been restricted to the
oxidometric determination of several compounds. This prompted us to undergo kinetic and mechanistic investigation.

Amino acids not only act as the building blocks in protein synthesis but also play a significant role in the metabolism. In metabolism, amino acids are subjected to many reactions and can supply precursors for many endogenous substances e.g. hemoglobin in blood. Amino acids can undergo many kinds of reactions, depending on whether a particular amino acid contains non-polar group or polar substituents. L-arginine, (L-Arg), one of the essential amino acids, is most important to life especially to the growth of the children. L-arginine plays an important role in mammals in the synthesis of urea, the principal form in which these species excrete nitrogen. It also finds applications in medicine and pharmaceuticals.

In the present work, the kinetics of oxidation of L-arginine by N-bromosuccinimide in presence of mercury(II) acetate in perchloric acid medium have been studied with a view to elucidate the mechanism of the reaction and to identify the reactive species of the oxidant in acid medium.

EXPERIMENTAL

Materials

Reagent grade chemicals and doubly distilled water were used throughout this work. A stock solution of N-bromosuccinimide was prepared by dissolving a known
mass of N-bromosuccinimide (SRL) in water. The concentration of the solution was verified by titration with standard sodium thiosulphate iodometrically\(^3\) using starch as an indicator. Series of stock solutions of L-arginine (sd fine-chem) and mercuric acetate were prepared by dissolving the appropriate amounts of samples in doubly distilled water. The succinimide was prepared\(^6\) and recrystallised by a known method as follows: a known amount of succinic acid is taken into a round bottom flask and concentrated ammonia solution was added slowly with cooling and shaking. Most of the acid dissolves forming a clear solution of ammonium succinate. The mixture was heated gently with a free flame and then strongly. The ammonium succinate commences to decompose with evolution of ammonia and succinimide was collected in the flask. The crude succinimide was crystallised. Its solution was prepared by dissolving a known amount of succinimide in distilled water.

Sodium thiosulphate (Fischer) was prepared in water. It was standardised\(^7\) against potassium iodate as follows: to the potassium iodide solution containing 1.0 mol dm\(^{-3}\) sulphuric acid in iodine flask a known volume of standard potassium iodate solution was added. The liberated iodine was titrated against sodium thiosulphate using starch as an indicator. Sodium perchlorate which was found to be inactive was used to maintain constant ionic strength and perchloric acid (BDH, AR) was used to get the required acidity.
KINETIC PROCEDURE:

All kinetic runs were carried out under pseudo-first order conditions at 26.0 ± 0.1°C unless otherwise stated. The [L-Arg] was at least ten fold excess over [NBS] containing 0.02 mol dm⁻³ Hg(OAc)₂. The first solution contained the required concentrations of substrate (L-arginine), perchloric acid, sodium perchlorate and mercuric acetate, the second solution was that of oxidant (NBS), of required concentration. One of the reaction solutions was added to the other. The progress of the reaction was followed by iodometric determination of unreacted NBS as follows. 5.0 cm³ of reaction mixture was pipetted out into an iodine flask containing 5.0 cm³ of 5% potassium iodide solution and a required amount of 2 mol dm⁻³ sulphuric acid was added, the iodine liberated by NBS was titrated against standard sodium thiosulphate solution using starch as an indicator. Such titrations were carried out at regular intervals of time and an example run is shown in Table II (i) (p.38). The first order rate constants (k_{obs}) were evaluated by the plots of log [NBS] versus time. Such plots in almost all cases were linear upto 90% completion of reaction; k_{obs} values were reproducible within ± 5%. No effect of dissolved oxygen on the rate of reaction was obtained.
Table II (i)

N-bromosuccinimide oxidation of L-arginine in aqueous acidic medium at 26° C.

**Example Run**

\[
\begin{align*}
[NBS] &= 1.0 \times 10^{-3}; \\
[H^+] &= 1.0 \times 10^{-3}; \\
\text{[Hg(OAc)\textsubscript{2}]} &= 0.02; \\
I &= 0.30 / \text{mol dm}^{-3} \\
\text{[L-Arg]} &= 5.0 \times 10^{-2};
\end{align*}
\]

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Burette Reading (cm\textsuperscript{3})</th>
<th>[NBS] x 10\textsuperscript{4} (mol dm\textsuperscript{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.6</td>
<td>9.6</td>
</tr>
<tr>
<td>3</td>
<td>9.2</td>
<td>9.2</td>
</tr>
<tr>
<td>5</td>
<td>8.4</td>
<td>8.4</td>
</tr>
<tr>
<td>10</td>
<td>7.7</td>
<td>7.7</td>
</tr>
<tr>
<td>20</td>
<td>5.3</td>
<td>5.3</td>
</tr>
<tr>
<td>30</td>
<td>4.3</td>
<td>4.3</td>
</tr>
<tr>
<td>40</td>
<td>3.2</td>
<td>3.2</td>
</tr>
<tr>
<td>50</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>60</td>
<td>1.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>
RESULTS

Stoichiometry and products analysis:

Stoichiometric studies were carried out under different sets of reaction mixtures containing different amounts of NBS and L-arginine at constant concentration of \([H^+]\) and ionic strength were kept to react for about 24 hours at 26 ± 1° C in an inert atmosphere. After the elapse of the reaction time, when \([\text{NBS}] > [\text{L-Arg}]\), the remaining NBS was assayed iodometrically as mentioned earlier. The oxidation products were identified as succinimide\(^9\) and aldehyde\(^10\) by their respective spot tests. The product, succinimide, was detected by the method as follows \(^9\): one or two drops of test solution is taken to dryness in a micro test tube along with a drop or two of concentrated hydrochloric acid. The excess acid is driven off by heating to 120° C. To detect any resulting ammonium chloride, a drop of 1N alkali is added to the residue and the mouth of the tube is covered with a piece of filter paper moistened with Nessler’s reagent. Qualitative filter paper must be used because almost all quantitative papers contain ammonium salts. The development of a brown or yellow stain on gentle warming indicates the presence of imides. And the presence of 4-guanidinobutaraldehyde was also confirmed by silver mirror test. The results are in agreement with 1:1 stoichiometry, (equation 1) as shown in Table II (ii) (p.40).
Table II (ii)

Stoichiometry* of N-bromosuccinimide oxidation of L-arginine in aqueous acidic medium at 26° C.

\[ [H^+] = 0.10; \quad [\text{Hg(OAc)}_2] = 0.02; \quad I = 0.30/\text{mol dm}^3. \]

<table>
<thead>
<tr>
<th>[NBS] x 10³</th>
<th>[L-Arg] x 10³</th>
<th>[NBS] x 10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taken</td>
<td>Taken</td>
<td>Found</td>
</tr>
<tr>
<td>3.0</td>
<td>1.0</td>
<td>2.01</td>
</tr>
<tr>
<td>4.0</td>
<td>2.0</td>
<td>2.04</td>
</tr>
<tr>
<td>5.0</td>
<td>3.0</td>
<td>2.03</td>
</tr>
<tr>
<td>6.0</td>
<td>4.0</td>
<td>2.02</td>
</tr>
<tr>
<td>8.0</td>
<td>6.0</td>
<td>2.03</td>
</tr>
</tbody>
</table>

Error ± 5%

*All concentrations are in mol dm⁻³.
The reaction orders were determined from the slopes of log $k_{obs}$ versus log concentration plots by varying the concentration of oxidant, reductant and acid in each, while keeping others constant.

**Effect of [N-bromosuccinimide]**

Keeping constant concentration of L-arginine, perchloric acid and sodium perchlorate as given in Table II (iii) (p.42), the concentration of [NBS] was varied in the range of $0.3 \times 10^{-3}$ to $5.0 \times 10^{-3}$ mol dm$^{-3}$. The constancy in the rate constants ($k_{obs}$) values and linearity of plots of log [NBS] versus time over more than 90% completion of the reaction as shown in Fig II (i) (p.43) indicates the order in [NBS] as unity.
Table II (iii)

Effect of variation of [NBS] on N-bromosuccinimide oxidation of L-arginine in aqueous acidic medium at 26° C.

\[
[L-\text{Arg}] = 2.0 \times 10^{-2}; \quad [H^+] = 0.10; \\
[Hg(OAc)_2] = 0.02; \quad I = 0.30 \text{ /mol dm}^{-3}.
\]

<table>
<thead>
<tr>
<th>([\text{NBS}] \times 10^3) (mol dm(^{-3}))</th>
<th>(k_{\text{obs}} \times 10^4) (s(^{-1}))</th>
<th>Expt*</th>
<th>Calc*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>2.93</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>2.90</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>2.95</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>2.95</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>2.85</td>
<td>3.07</td>
<td></td>
</tr>
</tbody>
</table>

*Experimental and Calculated.
First order plots of [NBS] on N-bromosuccinimide oxidation of L-arginine in aqueous acidic medium at 26°C.

(Conditions as in Table II (iii) (p.42))
**Effect of [L-arginine]**

The substrate, L-arginine was varied in the range of $3.0 \times 10^{-3}$ to $3.0 \times 10^{-2}$ mol dm$^{-3}$ at 26° C, keeping all other reactant concentrations and conditions constant (Table II (iv) (p.45)). The order in [L-arginine] was found to be less than unity as shown in Figure II (ii) (p.46).

**Effect of [perchloric acid]**

At constant concentration of oxidant, reductant and ionic strength, the [H$^+$] was varied in the range of 0.05 to 0.5 mol dm$^{-3}$ as given in Table II (iv) (p.45). The rate decreased with increase in [H$^+$]. The order was obtained by the plot of log $k_{obs}$ versus log [H$^+$] and is found to be an inverse fractional (Fig II (ii) (p.46)).

**Effect of [sodium perchlorate]**

Ionic strength (I) of the reaction was varied from 0.3 to 2.5 mol dm$^{-3}$ by varying concentration of sodium perchlorate in the reaction mixture keeping all the reactants concentration constant as given in Table II (v) (p.48). It was found that the rate of reaction is independent of ionic strength of the medium as shown in Table II (v) (p.48).
Table II (iv)

Effect of variation of [H+] and [L-Arg] on N-bromosuccinimide Oxidation of L-arginine in aqueous acidic medium at 26° C.

\[
[NBS] = 1.0 \times 10^{-3}; \quad [\text{Hg(OAc)}_2] = 0.02; \quad I = 0.30 /\text{mol dm}^3.
\]

<table>
<thead>
<tr>
<th>[H+] (mol dm(^{-3}))</th>
<th>[L-Arg] x 10(^2) (mol dm(^{-3}))</th>
<th>(k_{\text{obs}} \times 10^4) (s(^{-1}))</th>
<th>Expt.</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>2.0</td>
<td>3.69</td>
<td>3.80</td>
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</tr>
<tr>
<td>0.07</td>
<td>2.0</td>
<td>3.38</td>
<td>3.47</td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>2.0</td>
<td>2.95</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>0.30</td>
<td>2.0</td>
<td>1.60</td>
<td>1.73</td>
<td></td>
</tr>
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<td>0.50</td>
<td>2.0</td>
<td>1.20</td>
<td>1.21</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
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</tr>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>1.80</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>2.0</td>
<td>2.95</td>
<td>3.07</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>2.5</td>
<td>3.55</td>
<td>3.57</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>3.0</td>
<td>3.96</td>
<td>4.00</td>
<td></td>
</tr>
</tbody>
</table>
Figure II (ii)

Order in [L-Arg] and [H\(^+\)] on N-bromosuccinimide oxidation of L-arginine in aqueous acidic medium at 26°C

(Conditions as in Table II (iv) (p.45))
Effect of dielectric constant

The effect of changing the dielectric constant in the reaction medium was studied by adding acetic acid from 5% to 30% in the reaction medium at constant concentration of other reactants. Attempts to measure the relative permittivity (D) failed. However, they were computed from the values of pure liquids as in earlier work\textsuperscript{11}. The dielectric constants of the reaction medium at various compositions of water and acetic acid were calculated by using following equation at constant ionic strength and other reactant concentrations.

\[ D = D_1 V_1 + D_2 V_2 \]

where \( V_1 \) and \( V_2 \) are volume fractions and \( D_1 \) and \( D_2 \) are dielectric constants of water and acetic acid as 78.5 and 6.15 at 25 \( ^\circ \)C respectively. It was also confirmed that there was no reaction between acetic acid and N-bromosuccinimide at the experimental conditions employed. The dielectric constant effect was found to be negligible on the rate of reaction as shown in Table II (v) (p.48).
Table II (v)

Effect of ionic strength (I) and solvent polarity (D) on N-bromosuccinimide oxidation of L-arginine in aqueous acid medium at 26°C.

\[
\begin{align*}
[NBS] &= 1.0 \times 10^{-3}; \\
[L-\text{Arg}] &= 2.0 \times 10^{-2}; \\
[H^+] &= 0.10; \\
[Hg(OAc)_2] &= 0.02; \\
I &= 0.30 \text{ /mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>I</th>
<th>(k_{obs} \times 10^4)</th>
<th>% of HAc*-D</th>
<th>(k_{obs} \times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mol dm(^{-3}))</td>
<td>(s(^{-1}))</td>
<td>water(v/v)</td>
<td>(s(^{-1}))</td>
</tr>
<tr>
<td>0.3</td>
<td>2.81</td>
<td>5</td>
<td>74.9</td>
</tr>
<tr>
<td>0.6</td>
<td>2.87</td>
<td>10</td>
<td>71.3</td>
</tr>
<tr>
<td>1.0</td>
<td>2.84</td>
<td>15</td>
<td>67.6</td>
</tr>
<tr>
<td>1.5</td>
<td>2.87</td>
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<td>64.1</td>
</tr>
<tr>
<td>2.0</td>
<td>2.96</td>
<td>25</td>
<td>60.4</td>
</tr>
<tr>
<td>2.5</td>
<td>2.90</td>
<td>30</td>
<td>59.0</td>
</tr>
</tbody>
</table>

*Acetic acid.
Effect of mercury (II) acetate

The effect of concentration of mercury(II) acetate observed in the range of 0.02 to 0.1 mol dm$^{-3}$, keeping all other reactants concentrations constant as shown in Table II (vi) (p.50). It was found that there is a negligible effect on the rate of reaction as given in Table II (vi) (p.50). The function of added mercuric acetate is therefore only to fix up Br$^-$ formed in the course of reaction as HgBr$_2$ or HgBr$_4^{2-}$.

Effect of added products

Effect of initially added product, succinimide was studied in the concentration range of 0.50 x 10$^{-3}$ to 10.0 x 10$^{-3}$ mol dm$^{-3}$, keeping all other reactants concentrations constant. It was found that the added product had negligible effect on rate of reaction, (Table II (vi) (p.50)

Test for free radicals

The reaction mixture containing acrylonitrile was kept for 24 hours in an inert atmosphere. On diluting the reaction mixture by methanol, we did not get any precipitate indicating the absence of free radical intervention in the reaction.

Effect of temperature

The rate of reaction was measured at different temperatures under varying the [L-Arg]. The rate of reaction increased with increase in temperature. The rate
Effect of initially added product, succinimide and effect of $[\text{Hg(OAc)}_2]$ on N-bromosuccinimide oxidation of L-arginine in aqueous acidic medium at 26° C.

$[\text{NBS}] = 1.0 \times 10^{-3}$; $[\text{L-Arg}] = 1.0 \times 10^{-2}$; $[\text{H}^+] = 0.10$; $I = 0.30$ /mol dm$^{-3}$.

<table>
<thead>
<tr>
<th>Succinimide x 10$^3$ (mol dm$^{-3}$)</th>
<th>Hg(OAc)$_2$ x 10$^2$ (mol dm$^{-3}$)</th>
<th>$k_{obs} \times 10^4$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.0</td>
<td>2.72</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>2.79</td>
</tr>
<tr>
<td>4.0</td>
<td>2.0</td>
<td>2.76</td>
</tr>
<tr>
<td>7.0</td>
<td>2.0</td>
<td>2.85</td>
</tr>
<tr>
<td>10.0</td>
<td>2.0</td>
<td>2.91</td>
</tr>
<tr>
<td>--</td>
<td>2.0</td>
<td>2.56</td>
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<td>6.0</td>
<td>2.63</td>
</tr>
<tr>
<td>--</td>
<td>8.0</td>
<td>2.70</td>
</tr>
<tr>
<td>--</td>
<td>10.0</td>
<td>2.73</td>
</tr>
</tbody>
</table>

Error ± 5%.
constant, $k$, of the slow step of the scheme 1 were obtained from the intercept of $1/k_{obs}$ versus $1/[L\text{-Arg}]$ for different temperatures. The values of $k$ (dm$^3$ mol$^{-1}$s$^{-1}$) were found to be $1.0 \times 10^3$, $4.5 \times 10^3$ and $10 \times 10^3$ at 26, 31 and 36° C respectively and these values are incorporated in the Table II (vii) (p.52).

The activation parameters for the reaction were studied by using linear regression analysis (also know as the method of least square)$^{12}$. In generalised notation, the formula for the straight line is $y = ax + b$. The most tractable form of linear regression analysis assumes that values of the independent variables $'x'$ are known without error and that experimental error is manifested only in values of the dependent variable $'y'$. Most sets of kinetic data approximate this situation, in as much as times of observation are more accurately measurable than the chemical or physical quantities related to reactant concentrations. The straight line selected by common linear regression analysis is that which minimises the sum of the squares of the derivations of the $y$ variable from the line.

The slope $'a'$ and intercept $'b'$ parameters for the above equation can be calculated by linear regression analysis by any of several mathematically equivalent but different looking experiments. Most familiar are

\[
\text{Slope: } a = \frac{n \sum xy - \sum x \sum y}{n \sum x^2 - (\sum x)^2}
\]

\[
\text{Intercept: } b = \frac{\sum y - ax \sum x}{n \sum x^2 - (\sum x)^2}
\]
Table II (vii)

Effect of temperature on the slow step of the mechanism on N-bromosuccinimide Oxidation of L-arginine in aqueous acidic medium at 26° C.

\[
\begin{align*}
[NBS] &= 1.0 \times 10^{-3}; \\
[H^+] &= 0.10; \\
[Hg(OAc)] &= 0.02; \\
I &= 0.30/\text{mol dm}^{-3}.
\end{align*}
\]

<table>
<thead>
<tr>
<th>T* (K)</th>
<th>(k \times 10^3) (s(^{-1}))</th>
<th>(1/T \times 10^3) (K(^{-1}))</th>
<th>(\log k)</th>
<th>(Y_{\text{calc}}^{**})</th>
</tr>
</thead>
<tbody>
<tr>
<td>299</td>
<td>1.0</td>
<td>3.34</td>
<td>-3.00</td>
<td>-2.9703</td>
</tr>
<tr>
<td>304</td>
<td>4.5</td>
<td>3.28</td>
<td>-2.39</td>
<td>-2.4185</td>
</tr>
<tr>
<td>309</td>
<td>10.0</td>
<td>3.23</td>
<td>-2.00</td>
<td>-1.9648</td>
</tr>
</tbody>
</table>

*Temperature. **Calculated.
Where \( n \) is the no. of data points and the summation are for all data points in the set. These data were subjected to least square analysis and are given in Table II (vii) (p.52).

The activation parameters were evaluated from the plot of \( \log k \) versus \( 1/T \) as shown in Figure II (iii) (p.54) and are tabulated in Table II (viii) (p.55). The activation energy of the reaction was calculated by,

\[
E_a = -2.303 \times R \times \text{slope}
\]

The entropy of activation is calculated by

\[
\frac{\Delta S^\#}{4.576} = \log k - 10.753 - \log T + \frac{E_a}{4.576T}
\]

Where \( k \) is in sec\(^{-1}\), temperature in absolute and \( E_a \) in calories.

The enthalpy of activation is calculated by

\[
\Delta H^\# = E_a - RT
\]

And the free energy of activation was calculated by

\[
\Delta G^\# = \Delta H^\# - T \Delta S^\#
\]
Figure II (iii)

Effect of temperature on the slow step of the mechanism on N-bromosuccinimide oxidation of L-arginine in aqueous acidic medium at 26° C.

(Conditions as in Table II (vii) (p. 52))
Table II (viii)

Thermodynamic activation parameters for the N-bromosuccinimide oxidation of L-arginine in aqueous acidic medium at 26°C.

<table>
<thead>
<tr>
<th>Activation Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_a$ (kJ mol$^{-1}$)</td>
<td>$86 \pm 2$</td>
</tr>
<tr>
<td>$\log A$</td>
<td>$14.5 \pm 0.5$</td>
</tr>
<tr>
<td>$\Delta H^\circ$ (kJ mol$^{-1}$)</td>
<td>$84 \pm 2$</td>
</tr>
<tr>
<td>$\Delta S^\circ$ (J K$^{-1}$mol$^{-1}$)</td>
<td>$-17 \pm 4$</td>
</tr>
<tr>
<td>$\Delta G^\circ$ (kJ mol$^{-1}$)</td>
<td>$78 \pm 3$</td>
</tr>
</tbody>
</table>
DISCUSSION

It is known\(^{13}\) that the probable reactive species of NBS in acid solution are \(>\text{NBr}, \text{HOBr}, >\text{N}^+ \text{HBr}, \text{H}_2\text{OBr}\). The reaction is first order in [NBS] and fractional order in [L-Arg], while inverse fractional order in [H\(^+\)]. The inhibition nature of addition of H\(^+\) ions on rate may be explained by assuming the equilibria (I \(\rightleftarrows\) II) to be present and that the unprotonated species (I) is the reactive one

\[
\begin{align*}
\text{CH}_2\text{-CO} & \quad \text{NBr} + \text{H}^+ \quad \text{CH}_2\text{-CO} \\
\text{CH}_2\text{-CO} & \quad \text{NH}^+\text{Br}
\end{align*}
\]

The order of less than unity in [L-Arg] reveals the possibility of involvement of complex formation in the reaction system pre-equilibrium. Attempts to obtain spectral evidence were in vain, and there was no appreciable change in spectra of L-arginine and NBS in presence of an acid. A feeble interaction is probably involved. However, evidence for complex formation is obtained kinetically by the plot of 1/\(k_{\text{obs}}\) versus 1/[L-Arg] (Fig. II (iv) (p.60)), which showed a positive intercept. Such complex formation between oxidant and substrate was observed in earlier studies\(^{14}\).

L-arginine in aqueous solution exists as zwitterion. However, in strongly acidic medium, it exists in the protonated form. It is known that NBS serves as a source of bromonium ion (Br\(^+\)) and undergoes a simple two-electron reduction.
leading to the formation of bromide ion, succinimide and the products of reaction. The NBS as a source of bromonium ion gives product Br⁻ in presence of mercuric acetate. The unprotonated NBS (discussed elsewhere) reacts with protonated L-arginine to form a complex which decomposes in a slow step followed by fast steps to give products as shown scheme 1.

\[
\begin{align*}
\text{CH}_2\text{CO} & \quad \text{NHBr} & \quad \text{K}_1 & \quad \text{CH}_2\text{CO} \\
\text{CH}_2\text{CO} & \quad \text{NBr} + \text{H}^+ & & \quad \text{CH}_2\text{CO} \\
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{CO} & \quad \text{NBr} + \text{R-CH-COOH} & \quad \text{K}_2 & \quad \text{Complex (C)} \\
\text{CH}_2\text{CO} & \quad \text{NH}_2 & & \\
\end{align*}
\]

\[
\begin{align*}
\text{Complex (C)} & \quad \text{k} & \quad \text{R} \quad \text{C}=\text{NH} + \text{CH}_2\text{CO} \\
\text{COOH} & & & \quad \text{NH} + \text{HBr} \\
\end{align*}
\]

\[
\begin{align*}
\text{R} & \quad \text{C}=\text{NH} + \text{H}_2\text{O} & \quad \text{fast} & \quad \text{R-CHO} + \text{NH}_3 + \text{CO}_2 \\
\text{COOH} & & & \\
\end{align*}
\]

**Scheme 1**

The rate law of scheme 1 may be derived as follow,

\[
\text{Rate} = k [C]
\]
The total \([\text{L-Arg}]_T\) is given by

\[\text{[L-Arg]}_T = \text{[L-Arg]}_f + \text{[C]}\]

\[= \text{[L-Arg]}_f + K_2 \text{[NBS]} \text{[L-Arg]}_f\]

\[= \text{[L-Arg]}_f \{1 + K_2 \text{[NBS]}\}\]

Therefore

\[\text{[L-Arg]}_f = \frac{\text{[L-Arg]}_T}{1 + K_2 \text{[NBS]}} \quad (3)\]

Similarly,

\[\text{[NBS]}_T = \text{[NBS]}_f + \text{[NBS]}^+ + \text{[C]}\]

\[= \text{[NBS]}_f + K_1 \text{[NBS]} \text{[H]}^+ + K_2 \text{[NBS]} \text{[L-Arg]}\]

\[= \text{[NBS]}_f \{1 + K_1 \text{[H]}^+ + K_2 \text{[L-Arg]}\}\]

Therefore

\[\text{[NBS]}_f = \frac{\text{[NBS]}_T}{1 + K_1 \text{[H]}^+ + K_2 \text{[L-Arg]}} \quad (4)\]

Substituting the values of equation (3) and (4) in equation (2) we get

\[\text{Rate} = \frac{k K_2 \text{[NBS]}_T \text{[L-Arg]}_T}{1 + K_2 \text{[NBS]} (1 + K_1 \text{[H]}^+ + K_2 \text{[L-Arg])}} \quad (5)\]
In view of low concentration of NBS used, the term $1 + K_2 \left[NBS\right]$ approximated to unity then the above equation (5) reduces to

$$\frac{\text{Rate}}{[\text{NBS}]} = \frac{k_{\text{obs}} \cdot k_2 \cdot [\text{L-Arg}]}{1 + K_1 \left[H^+\right] + K_2 \cdot [\text{L-Arg}]}$$

(6)

The mechanism of scheme 1 and the rate law (6) may be verified by rearranging it in the form (7)

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k \cdot k_2 \cdot [\text{L-Arg}]} + \frac{K_1 \left[H^+\right]}{k \cdot k_2 \cdot [\text{L-Arg}]} + \frac{1}{k}$$

(7)

According to equation (7) the plots of $1/k_{\text{obs}}$ versus $1/[\text{L-Arg}]$ and $1/k_{\text{obs}}$ versus $[H^+]$ are linear with non zero intercepts which are verified in Figure II (iv) (p.60). From slopes and intercepts of such plots $k$, $K_1$ and $K_2$ values are obtained at $26^\circ\text{C}$ as $1.0 \times 10^{-3} \text{ s}^{-1}$, 12.5 mol dm$^{-3}$ and 50.0 dm$^3$ mol$^{-1}$ respectively. Using these values the calculated rate constants are in reasonable agreement with the experimental values as given in Table II (iii) (p.42) and Table II (iv) (p.45).

The negligible effect of ionic strength and dielectric constant might be due to involvement of neutral species in the reaction. The modest energy of activation and entropy of activation suggest the involvement of complex transition state in the reaction$^{15}$. 

59
Verification of rate law (6) in the form of (7) on N-bromosuccinimide Oxidation of L-arginine in aqueous acidic medium at 26°C.

(Conditions as in Table II (iv) (p.45))
Findings

N-bromosuccinimide oxidation of L-arginine in aqueous perchloric acid medium is a pseudo-first order reaction with negative dependency on perchloric acid concentration and has 1:1 stoichiometry. The active species of NBS in acid solution are as >NBr, HOBr, N'\text{HBr}, H_2OBr. However in the present kinetic study, the unprotonated species N'\text{HBr} is found to be the reactive one. The product 4-guanidinobutaraddehyde is confirmed. Addition of mercuric (II) acetate is only to fix up Br⁻ formed in the course of reaction as HgBr₂ or HgBr₄²⁻. The reaction constants involved in the mechanism are evaluated.

Importance of chapter II

The main products of the reaction were found to be succinimide and the corresponding aldehyde i.e 4-guanidinobutaraldehyde. A mechanism in terms of active species of oxidant is proposed and the rate law is derived and verified.
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