Kinetic Study of the Reaction between Ammonia and Chlorine

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Kinetic studies of the reaction between Ammonia and Chlorine were carried out and it was found to be of second order. The reaction was studied at 20 ± 0.1 °C and below pH value of 5. Above this pH the reaction being very fast could not be measured. The ΔE (energy of activation) and AS (entropy of activation) values of this reaction were found to be 32.66 Kcal/mole and 10.23 cal/deg.mole respectively. The reactive species appears to be hypochlorite in this reaction.

Ammonia has been estimated by chlorine by visual titration method \(^1-^4\), but no work seems to have been done on its kinetic studies with chlorine. The kinetics of the reaction of ammonia with bromine has been studied by Grover and Mehrotra \(^5\). Here, the reaction has been studied with special reference to the effect of hydrogen ion concentration. The investigation shows that the reaction is of second order and may be expressed by the following equation:

\[ 2 \text{NH}_3 + 3 \text{Cl}_2 \rightarrow \text{N}_2 + 6 \text{HCl}; \]

or

\[ 2 \text{NH}_3 + 3 \text{ClO}^- \rightarrow \text{N}_2 + 3 \text{Cl}^- + 3 \text{H}_2\text{O}. \]

**Materials required:** Ammonium chloride used was E. Merck G.R. quality and all other chemicals employed were B.D.H. AnalAR products. The solutions used were hyp (0.0025 N), chlorine (0.0125 M) and ammonium chloride (0.025 M) except in case of experiments using excess of chloride.

**Procedure:** To 25 ml of 0.0125 M chlorine solution was added the requisite quantity of buffer solution. After keeping it for half an hour in the constant temperature bath, an equivalent quantity (to that of hypochlorite present) of 0.025 N solution of ammonium chloride (which had been kept at the same temperature of the bath for about half an hour) was added to it (except in case of use of excess of chlorine) and the volume made up to 100 ml. The timer was started during the mixing. Samples (10 ml) were removed at known intervals of time and quenched by addition of 10 ml of 0.1 N KI and 15 ml N H\textsubscript{2}SO\textsubscript{4}. After 10 min, the iodine liberated was titrated against 0.0025 N sodium thiosulphate solution using starch as indicator. The difference between the two titre values (i.e. of blank and that of reaction mixture) at definite intervals of time represented the amount of substance oxidised at a particular stage.

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**Reaction rate:** Table 1 indicates the results obtained with excess of chlorine at 20 ± 0.1 °C. It shows that the order of reaction in this case is unity — the overall order being two. In this case a plot of \(\log(a-x)\) against time in minutes was found to be a straight line from whose slope \(k_1\) (first order constant) was calculated.

Studies on the effect of different concentrations of ammonium chloride could not be conducted in these cases as the reaction was completed within a few minutes in presence of a high concentration of ammonium chloride.

**Second order constants using equivalent concentrations of reactants under different conditions**

On plotting the values of \(1/a-x\) against time in minutes, a straight line was obtained in these cases. Thus from the slope, the value of \(k_2\) (second order constant) was obtained and the results of these investigations are summarised in Table 2 A.

At 20 ± 0.1 °C, beyond pH 4.7, the reaction was found to be very fast and therefore it could not be measured easily. In this table the data (at serial Nos. 3, 6 and 7) was used for the calculation of the temperature coefficient of the reaction at temperatures 20, 15 and 10 °C as shown in Table 2 B.

**Results and Discussions**

**Order of reaction**

The oxidation of ammonium chloride by chlorine has been shown to be of second order. The reaction between chlorine and ammonium chloride has been shown to be of first order with respect to ammonium chloride — the total order being two. However, in case of ammonium chloride, kinetic studies using excess of reductant could not be conducted due to analytical difficulties.

**Effect of pH**

In the case of reaction of ammonia and chlorine, the rate constant goes on increasing with the
rise of pH and the reaction becomes very fast beyond pH 5.

Table 1. Reaction of ammonium chloride with excess of chlorine. Temperature = 20 ± 0.1 °C; Mean pH = 4.20; Hypo = 0.01 N.

<table>
<thead>
<tr>
<th>No.</th>
<th>Temperature [°C]</th>
<th>pH</th>
<th>K [sec⁻¹ mole⁻¹ l × 10⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>20 ± 0.1</td>
<td>3.5</td>
<td>147.30</td>
</tr>
<tr>
<td>2.</td>
<td>20 ± 0.1</td>
<td>3.8</td>
<td>149.70 (used HClO instead of NaClO)</td>
</tr>
<tr>
<td>3.</td>
<td>20 ± 0.1</td>
<td>4.45</td>
<td>1346.00</td>
</tr>
<tr>
<td>4.</td>
<td>20 ± 0.1</td>
<td>4.30</td>
<td>1251.70 (in presence of 25 ml 0.1 m Na₂SO₄)</td>
</tr>
<tr>
<td>5.</td>
<td>20 ± 0.1</td>
<td>4.70</td>
<td>846.30 (in presence of 25 ml 0.1 m CH₃COONa)</td>
</tr>
<tr>
<td>6.</td>
<td>15 ± 0.1</td>
<td>4.25</td>
<td>845.90</td>
</tr>
<tr>
<td>7.</td>
<td>10 ± 0.1</td>
<td>4.20</td>
<td>307.70</td>
</tr>
</tbody>
</table>

Table 2 A. Second order constants using equivalent concentrations of reactants at different temperatures.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>K [sec⁻¹ mole⁻¹ l × 10⁻³]</th>
<th>Temperature coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>307.70</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>845.90</td>
<td>2.75(10−15°C)</td>
</tr>
<tr>
<td>20</td>
<td>1346.00</td>
<td>1.59(15−20°C)</td>
</tr>
</tbody>
</table>

Effect of added electrolytes

The data in Table 2A show that the effect of added electrolytes, like sodium sulphate and sodium acetate, is negative, and that their rates are influenced by the presence of the anions like sulphate and acetate. Thus, the anion of this compound is the probable reactive species in this case against hypochlorous acid, molecular chlorine, or hypochlorite anion from chlorine solutions.

Thermodynamic parameters

The higher values of energy of activation (above 20 Kcal/mole) of ammonium chloride (E = 32.66) indicates the presence of a higher order in this case. Beside this, this high positive values of entropy of activation (ΔS = 10.23) of ammonia suggests that the reaction is taking place between oppositely charged ions viz. ammonium cation (NH₄⁺) and hypochlorite anion (ClO⁻).

Reactive species

Chlorate has not been found to react in slightly acidic, neutral or alkaline solution in which medium the reaction under study has been found to be fast. In case of ammonia the rate goes on increasing with increasing pH and, thus, an equilibrium between the remaining oxidising components viz., HClO, ClO⁻, Cl₂ and Cl₃⁻ can be considered.

Taking into consideration, the formation of the ions mentioned above, we have,

\[
[HClO] + [ClO⁻] + [Cl₂] + [Cl₃⁻] = 1.5626 \times 10^{-3},
\]

(at the middle stage of the reaction)

Out of the above reaction species, [ClO⁻] is maximum at high values of pH, which is applicable in this case.

Chlorine solutions contain [HClO], [ClO⁻], [Cl₂] and [Cl₃⁻]. Theoretical considerations show that in chlorine solutions HClO concentration is maximum at pH 4 to 5, [ClO⁻] at pH 9 to 12 and [Cl₂] and [Cl₃⁻] at pH 2 in the pH range studied (pH 2 to 12).

The reaction between ammonia and chlorine was found to become very fast with increasing pH. It was assumed that like the case of serine, here, also, the reactive species may be hypochlorite anion (ClO⁻). Besides, it was not possible to compare these results with the calculated values of concentrations of different species present in the reaction mixture as the rate constants could not be recorded beyond pH 5. The reaction may be deemed to take place between the hypochlorite anion (ClO⁻) and the ammonium cation (NH₄⁺) and can be represented as under:

\[
2 \text{NH}_4^+ + 3 \text{ClO}^- \rightarrow \text{N}_2 + 3 \text{Cl}^- + 3 \text{H}_2\text{O} + 2 \text{H}^+.
\]

This view is supported by the fact that in terms of collision theory, reactions between oppositely charged ions are more rapid than predicted by theory and that the value of entropy of activation in this case is positive.

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1 K. C. Grover, J. Res. (Sci.) Agra Univ. 4, 627 [1955].
3 F. Oberhauser, Z. anorg. Chem. 144, 257 [1925].