

Kinetics of Oxidation of α -Alanine by N-Bromosuccinimide

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The kinetics of oxidation of α -alanine by N-bromosuccinimide has been studied voltammetrically. The specific reaction rate is $70.00 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C . The energy of activation, frequency factor and entropy of activation are found to be $13.40 \text{ kJ mol}^{-1}$, $1.563 \times 10^4 \text{ s}^{-1}$ and $-172.94 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The specific reaction rate is influenced by hydrogen ion concentration and dielectric constant of the medium. The most probable mechanism has been suggested.

Key Words: Kinetics, Oxidation, α -Alanine, N-Bromosuccinimide.

INTRODUCTION

N-Bromosuccinimide (NBS) is a potent oxidant and has been used in the quantitative determinations¹⁻³. It is a source of positive halogen and has been exploited as an oxidant for a variety of substrates in both acidic and alkaline medium⁴⁻⁹.

In recent years, studies of oxidation of various organic compounds by N-halocompounds¹⁰⁻¹⁶ have attracted considerable attention¹⁷⁻²⁰. Although the NBS oxidation of large variety of amino acids have been studied, there seems to be no report on voltametric oxidation of α -alanine by NBS.

In present study, we have carried out a voltametric oxidation of α -alanine by NBS using rotating platinum electrode (RPE) technique. At a potential of 0.0 volt vs. saturated calomel electrode (SCE) applied at the RPE, only NBS yields diffusion current proportional to its concentration, whereas neither the α -alanine nor the product of the reaction yields any diffusion current. Therefore the course of the reaction can be followed by monitoring the concentration of the unreacted NBS from the measurement of the diffusion current at various intervals of time.

EXPERIMENTAL

Pure N-bromosuccinimide (NBS) was obtained by crystallization²¹ from water at maximum temperature of 75°C . Its stock solution of $1.0 \times 10^{-2} \text{ M}$ was prepared and standardized by iodometric method^{22,23}. Similarly, stock solution of $1.0 \times 10^{-2} \text{ M}$ each of α -alanine and potassium chloride were prepared.

For the experimental work, the required volumes of the stock solutions were diluted to obtain the following solutions.

Solution A: 4.0×10^{-4} M α -alanine + 1.0×10^{-3} M potassium chloride.

Solution B: 4.0×10^{-4} M NBS + 1.0×10^{-2} M potassium chloride.

All the solutions were kept in black coloured stoppered bottles and thermostated at the desired temperature.

Kinetic measurements: For the kinetic studies, the RPE and SCE were dipped into an empty 250 mL beaker. The RPE was rotated with the constant speed. The whole assembly was kept in a thermostat at 25 °C. 100 mL each of solution A and B was quickly poured into the beaker and stopwatch was simultaneously started. The resulting concentration each of α -alanine and NBS would be 2.0×10^{-4} M and that of potassium chloride 1.0×10^{-2} M. The galvanometer deflection (d) in cm proportional to the diffusion current, was noted at intervals of 10 s for several minutes. A plot of reciprocal of the deflection in cm against time in second showed a good straight line. By extrapolating this line to zero time, the deflection at zero time could be estimated and this deflection would correspond to initial concentration of NBS. From the corresponding diffusion current measurement, the remaining unreacted concentration of NBS during the progress of the reaction with respect to time could be estimated. The order, activation parameters were evaluated by measuring the specific reaction rate at various temperatures. Further the effect of dielectric constant of the medium was evaluated.

RESULTS AND DISCUSSION

During the course of the reaction, the concentrations of the unreacted NBS (a-x) at various instants have been evaluated. The plot of $1/(a-x)$ vs. time is satisfactorily linear, indicating that oxidation of α -alanine by NBS follows first order with respect to each reactant and hence is of overall second order. The slope of this curve is the specific reaction rate and is found to be $70.00 \text{ mol}^{-1} \text{ litre s}^{-1}$ at 25 °C.

The products of oxidation of α -alanine by NBS were identified as carbon dioxide, bromine, ammonia and acetaldehyde by their respective spot test²⁴. The activation parameters were evaluated by measuring the specific reaction rate at various temperatures ranging 15-45 °C (Table-1). The plot of $\log k$ vs. reciprocal of absolute temperature was satisfactorily linear. From slope the energy of activation was evaluated and was found to be $13.40 \text{ kJ mol}^{-1}$. Further the frequency factor, entropy of activation were also evaluated and the values are found to be $1.563 \times 10^4 \text{ s}^{-1}$ and $-172.94 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively (Table-2).

Each kinetic experiment was repeated three times and the results are reproducible within limits of $\pm 2 \%$. The error in the measurement of diffusion current is only about 1 %. The specific reaction rates were thus accurate to within $\pm 3 \%$ considering the various errors in the measurements.

TABLE-1
KINETICS OF OXIDATION OF α -ALANINE BY N-BROMOSUCCINIMIDE:
VARIATION OF THE SPECIFIC REACTION RATE WITH TEMPERATURE
Concentration of N-bromosuccinimide : 2.0×10^{-4} M; Concentration of
 α -alanine : 2.0×10^{-4} M; Concentration of acetic acid-water : 50 % (v/v);
Ionic strength of the reaction medium : 1.0×10^{-2} M

Temperature		$\frac{1}{T}/10^{-3} \text{K}^{-1}$	Specific reaction rate $k/\text{mol}^{-1} \text{ litre s}^{-1}$	log k
$t/^{\circ}\text{C}$	$T/^{\circ}\text{K}$			
15	288	3.472	58.50	1.767
25	298	3.356	70.00	1.845
35	308	3.247	84.00	1.924
45	318	3.145	98.80	1.995

Slope of the log k vs. $1/T$ curve = $-0.70 \times 10^3 \text{ K}$

Energy of activation for the reaction (E_a) = $13.40 \text{ kJ mol}^{-1}$

TABLE-2
KINETICS OF OXIDATION OF α -ALANINE BY N-BROMOSUCCINIMIDE:
ACTIVATION PARAMETERS AT 25°C

Activation parameters	Value
Specific reaction rate (k)	$70.00 \text{ mol}^{-1} \text{ litre s}^{-1}$
Energy of activation (E_a)	$13.40 \text{ kJ mol}^{-1}$
Frequency factor (A)	$1.563 \times 10^4 \text{ s}^{-1}$
Entropy of activation (ΔS^{\ddagger})	$-172.94 \text{ J mol}^{-1} \text{ K}^{-1}$

TABLE-3
KINETICS OF OXIDATION OF α -ALANINE BY N-BROMOSUCCINIMIDE:
EFFECT OF DIELECTRIC CONSTANT
Concentration of N-bromosuccinimide : 2.0×10^{-4} M; Concentration of
 α -alanine : 2.0×10^{-4} M; Ionic strength of the reaction medium : 1.0×10^{-2} M;
Temperature : 25°C

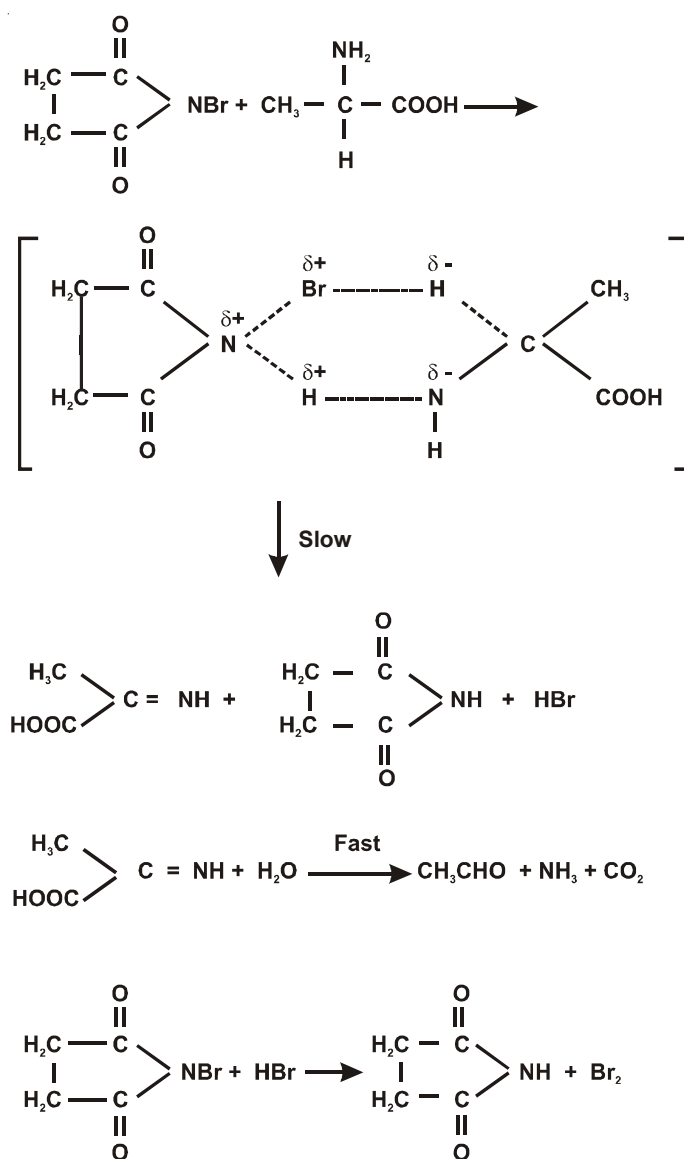
Acetic acid- water % (v/v)	Dielectric constant (D)	$\frac{D-1}{2D+1}/10^{-2}$	Specific reaction rate ($k/\text{mol}^{-1} \text{ litre s}^{-1}$)	log k
100-00	06.15	38.7	01.95	0.290
80-20	18.00	45.9	33.10	1.520
70-30	24.75	47.0	44.70	1.650
60-40	31.50	47.7	61.65	1.790
50-50	38.75	48.1	70.00	1.845

Mechanism: It was observed that the rate of reaction decreases with increasing the H^+ concentration. This may be due to the equilibrium between the protonated and unprotonated forms of the NBS. It indicates that the unprotonated form is reactive and not the protonated form. The rate of reaction decreases by changing the percentage of acetic acid-water

mixture from 50 to 100 % (Table-3) and the plot of $\log k$ vs. $(D-1)/(2D+1)$ gives a positive slope, indicating that the reaction must be of dipole-dipole type.

The absorption spectra of NBS in the presence and absence of α -alanine is found to be same which indicates that there is no complex formation between NBS and α -alanine under the present experimental conditions.

From the observed second order kinetics and reaction products such as acetaldehyde, carbon dioxide and bromine, the most probable mechanism for the oxidation of α -alanine by NBS could be



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