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Kinetics and Mechanism of the Oxidation of Glycine by N-Bromosuccinimide

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With 3 Figures

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A systematic kinetic study on the oxidation of glycine by N-bromosuccinimide (*NBS*) in presence of mercuric acetate in acetic acid—water media has been made. Near first order dependence in *NBS* and glycine and near inverse first order dependence in hydrogen ion concentrations have been observed. A negligible ionic strength effect and a positive dielectric effect have been observed. Various rate parameters have been computed and hydrocyanic acid identified as the end product. On the basis of the kinetic data, a mechanism of the reaction has been proposed.

Use of *NBS* as a titrimetric reagent for the oxidimetric determination of several compounds, both organic and inorganic, is well known[1, 2]. However, the literature lacks with a detailed step by step mechanism of oxidations by *NBS*. The present work incorporates a study on the kinetics and mechanism of oxidation of glycine by *NBS* in acetic acid—water media and a rate law in accord with the experimental data subsequently formulated.

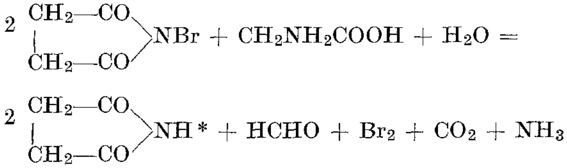
Experimental

All the reagents used were of highest purity available. G.R.S. Merck sample of *NBS* was prepared always fresh and the solution was stored in black Japan coated bottles and its strength was checked by iodometric method[3]. A.R., B.D.H. glycine and E. Merck (Germany) mercuric acetate was employed. Other reagents viz. glacial acetic acid, methanol, $NaClO_4$, $HClO_4$ and NaOH were of analaR grade. Jena glass stills were used and reaction stills blackened from outside. Triple distilled water was used throughout the course of investigations. A Leeds & Northrup pH meter was used for pH measurements. The reaction was studied in 70% glacial acetic acid and the pH of the reaction mixtures was always maintained at 1.0 by the addition of suitable amounts of alkali or perchloric acid as required.

All kinetic measurements were carried out at constant temperature (± 0.1 °C). The reaction was initiated by rapid addition of *NBS* to the mixture containing glycine—glacial acetic acid—mercuric acetate—water and mixing them by vigorous shaking. 5 ml of aliquots of the reaction mixtures were withdrawn at regular intervals of time and transformed quickly to titrating flasks containing 5 ml of 4% KI. The liberated iodine was estimated by standard $Na_2S_2O_3$ solution using starch as indicator.

Stoichiometry

The stoichiometry of the reaction was ascertained by carrying out several sets of experiments with varying amounts of *NBS* concentration largely in excess over glycine concentration. The results showed that one mole of glycine consumes two moles of *NBS*. It is well known that oxidation of glycine gives either formaldehyde or hydrocyanic acid. Accordingly, the following stoichiometric equations can be formulated:



$$2\left.\begin{matrix}CH_2\text{—}CO\\ |\\ CH_2\text{—}CO\end{matrix}\right\rangle NBr + CH_2NH_2COOH + H_2O =$$
$$2\left.\begin{matrix}CH_2\text{—}CO\\ |\\ CH_2\text{—}CO\end{matrix}\right\rangle NH^{*} + HCHO + Br_2 + CO_2 + NH_3 \qquad (1)$$

and

$$2\ NBS + CH_2NH_2COOH = 2\ BS + HCN + 2\ HBr + CO_2 \qquad (2)$$

In order to ascertain the exact stoichiometry between the above two possibilities, tests were performed for the identification of formaldehyde and hydrocyanic acid. Distinct and positive tests[4] for hydrocyanic acid were obtained and thus the stoichiometry is exactly represented by equation (2).

Results

Kinetic investigations were carried out at several initial concentrations of *NBS* and glycine, keeping other variable parameters constant (Table 1). First order dependence in *NBS* was followed at all initial concentrations of *NBS*. The pseudo-first order rate constants (k_1') in *NBS* were computed from the slopes of the log concentration vs. time plots (Fig. 1).

An increase in the pseudo-first order rate constants in *NBS* was observed with increase in glycine concentration. Further the order

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* *BS*.

in glycine, concentration was computed from the slopes of log k_1' vs. log [glycine] plots (Fig. 2) which gave orders as 0.87 and 0.89 at 35° and 40° resp., the average being 0.88.

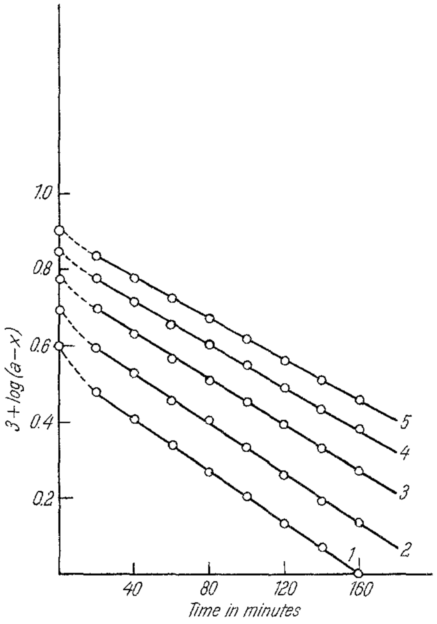


Fig. 1. First order rate plots for *NBS* variation at 35° [Glycine] = $1.0 \times \times 10^{-2} M$, [Mercurie acetate] = $2.0 \times 10^{-3} M$, pH = 1.0, [*NBS*] = 0.80, 1.00, 1.20, 1.40, and $1.60 \times 10^{-3} M$ in 1, 2, 3, 4, and 5 resp.

Table 1. *Effect of Reactants' Concentration on the Reaction Rate. [Mercuric Acetate]* = $2.0 \times 10^{-3} M$, *pH = 1.0*

$10^3 \cdot [NBS]$, M	$10^2 \cdot$ [Glycine], M	$k_1' \times 10^5$, sec^{-1}	
		35°	40°
0.80	1.00	13.2	21.1
1.00	1.00	12.4	20.4
1.20	1.00	11.6	12.5
1.40	1.00	11.0	18.8
1.60	1.00	10.4	18.2
1.00	0.50	6.67	11.0
1.00	0.75	9.52	16.3
1.00	1.50	17.2	29.4
1.00	2.00	21.7	35.9
1.00	2.50	26.3	44.9

The reaction was found to be very much susceptible to change in pH of the reaction mixture. Keeping other parameters constant, an increase in pH of the medium increased the rate of the reaction. The order in hydrogen ion concentration, calculated from the slopes of the plots of log k_1' vs. pH (Fig. 3) were found as 0.89 and 0.91 at 35 and 40° resp., the average being 0.90.

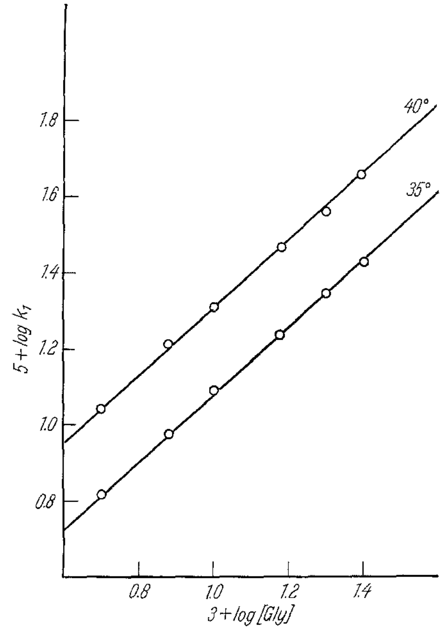


Fig. 2. Plot of log k_1' vs. log [Glycine] at 35 and 40°. [*NBS*] = $1.0 \times 10^{-3} M$, pH = 1.0, [Mercuric acetate] = $2.0 \times 10^{-3} M$

Table 2. *Effect of Sodium Perchlorate on the Reaction Rate* [*NBS*] = $1.0 \times 10^{-3} M$, [*Glycine*] = $1.0 \times 10^{-2} M$, [*Mercuric Acetate*] = $2.0 \times 10^{-3} M$, *pH = 1.0, Temp. = 35°*

[$NaClO_4$], $10^2 \cdot M$	$k_1' \times 10^5$ sec^{-1}
0	12.4
2	12.5
4	12.7
6	12.6
8	12.8

The effect of varying ionic strength by using varying amounts of sodium perchlorate was found to be negligible (Table 2) and thus revealed a zero ionic strength effect.

The reaction was also studied in different glacial acetic acid—water—methanol mixtures (Table 3). It was observed that the rate of the reaction is decreased pointing to a positive dielectric effect.

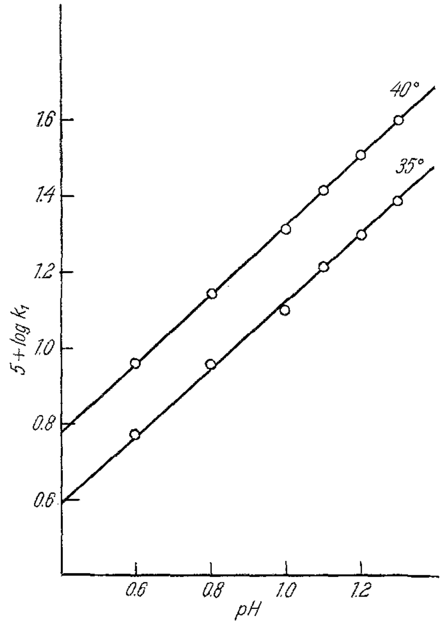


Fig. 3. Plot of log k_1' vs. pH at 35 and 40°, $[NBS] = 1.0 \times 10^{-3}M$, $[\text{Glycine}] = 1.0 \times 10^{-2}M$ and $[\text{Mercuric acetate}] = 2.0 \times 10^{-3}M$

Table 3. *Effect of Methanol on the Reaction Rate.* $[NBS] = 1.0 \times 10^{-3}M$, $[Glycine] = 1.0 \times 10^{-2}M$, $[Mercuric\ Acetate] = 2.0 \times 10^{-3}M$, $pH = 1.0$, *Temp.* = *35°*

Methanol, %	$k_1' \times 10^5$ sec^{-1}
0	12.4
4	11.7
8	10.9
12	10.1
16	9.37

To avoid any possible bromine oxidation, all these oxidative studies were made with mercuric acetate concentration more than that of *NBS*. Several rate parameters viz. temperature coefficient, energy of activation, frequency factor, heat of activation, entropy of activation and free energy of activation were computed from the rate study measurements carried out at six temperatures (30–55°), the average values being 2.65, 19.2 kcal mole^{-1}, 2.48×10^{10} sec^{-1}, 18.6 kcal mole^{-1}, — 12.0 cal deg.$^{-1}$ mole^{-1} and 22.3 kcal mole^{-1}, resp.

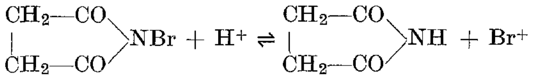
Discussion

It may be emphasised that all these oxidative studies have been made in presence of mercuric acetate (more than that of *NBS*), which simply means that Br_2 oxidation has been completely suppressed, which would have formed by the interaction of HBr and *NBS* as follows:

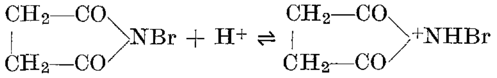
$$NBS + HBr \rightarrow BS + Br_2 \qquad (3)$$

Mercuric acetate acts as scavenger[5, 6] for any Br^- formed in the reaction and thus ensuring that oxidation takes place purely through *NBS*.

NBS is known to exist in acidic media in the following equilibria:



(4)



(5)

(*NBS*) $(\overset{+}{N}BSH)$

Thus *NBS* itself or Br^+ or protonated *NBS* may be the possible oxidising species[7–9].

Similarly glycine is known to exist in aqueous media as follows:

$$\overset{+}{N}H_3CH_2COOH \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} NH_2CH_2COOH \rightleftharpoons \overset{+}{N}H_3CH_2COO^-$$

*Gly*H$^+$ *Gly* (Zwitterion)

$$\underset{+H^+}{\overset{+H^+}{\rightleftharpoons}} \underset{Gly^-}{NH_2CH_2COO^-} \qquad (6)$$

Thus glycine or *Gly*H$^+$ (conjugate acid of glycine) or *Gly*$^-$ (conjugate base of glycine) may be the possible reducing species.

All the possibilities of reactions between the reducing species (*Gly*, *Gly*H$^+$, and *Gly*$^-$) and oxidising species (*NBS*, Br$^+$, and *NBS*H$^+$) have been explored and the following scheme has been found in agreement with the observed kinetic data wherein it is proposed that a *NBS* molecule attacks the conjugate base of glycine (*Gly*$^-$) in a slow step forming an intermediate complex which subsequently reacts with another molecule of *NBS* in a fast step leading to products. Thus

$$Gly \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Gly^- + \mathrm{H}^+ \qquad \text{(i)}$$

$$Gly^- + NBS \xrightarrow{k_2} X + \mathrm{Br}^- \quad \text{slow \& rate determining step} \qquad \text{(ii)}$$

$$X + NBS \xrightarrow{k_3} \text{Products} \quad \text{fast step} \qquad \text{(iii)}$$

Application of steady state treatment to the above scheme with reasonable approximation $k_{-1}\,[\mathrm{H}^+] \gg k_2\,[NBS]$ gives the rate law as:

$$-\frac{\mathrm{d}}{\mathrm{d}t}[NBS] = \frac{2k_1k_2}{k_{-1}}\,\frac{[NBS][Gly]}{[\mathrm{H}^+]} \qquad (7)$$

A negligible influence of ionic strength and a positive dielectric effect are in conformity with the above proposed mechanism. The observed stoichiometry (1 mole of glycine : 2 moles of *NBS*) is also in accord with the above mechanism.

Thus, in the oxidation of glycine by *NBS* in acidic media, it has been found that *NBS* itself is the oxidising species, and, the conjugate base of glycine (*Gly*$^-$) is the principal species reduced.

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