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# Kinetics and Mechanism of Oxidation of Allyl Alcohol by *N*-Bromosuccinimide

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The kinetics of oxidation of allyl alcohol by *N*-bromosuccinimide (*NBS*) has been studied at 35 °C in aqueous medium. The reaction shows first order dependence on both *NBS* and allyl alcohol. In fairly high acid concentration, there is no change in the rate of the reaction but at low acid concentration, the rate is considerably enhanced. There is no primary salt effect. At varying mercuric acetate concentrations, the rate constant remains the same. But in the absence of mercuric acetate, the rate is enhanced. The kinetic parameters, $E_a$, *Arrhenius* factor $A$, $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ have been calculated. A rate law in agreement with experimental results has been derived. A mechanism is proposed.

*(Keywords: Allyl alcohol; Kinetics; Mechanism; Oxidation)*

*Kinetik und Mechanismus der Oxidation von Allylalkohol mit N-Bromsuccinimid*

Die Kinetik der Oxidation von Allylalkohol mit *N*-Bromsuccinimid (*NBS*) wurde bei 35 °C in wäßrigem Medium untersucht. Die Reaktion zeigt erste Ordnung gegenüber *NBS* und Allylalkohol. Bei relativ hoher Säurekonzentration zeigt sich keine Änderung der Reaktionsgeschwindigkeit, bei niedriger Säurekonzentration wird die Reaktionsgeschwindigkeit beträchtlich erhöht. Es wurde kein primärer Salzeffekt festgestellt. Bei varriierender Quecksilberacetatkonzentration bleibt die Reaktionsgeschwindigkeit gleich, bei Abwesenheit von Quecksilberacetat wird jedoch die Geschwindigkeitskonstante erhöht. Die kinetischen Parameter, $E_a$, der *Arrhenius*faktor $A$, $\Delta H^{\ddagger}$, $\Delta G^{\ddagger}$ und $\Delta S^{\ddagger}$ wurden bestimmt. Ein Geschwindigkeitsgesetz in Übereinstimmung mit den experimentellen Befunden wurde abgeleitet und ein Mechanismus vorgeschlagen.

## Introduction

The kinetics of oxidation of a number of secondary alcohols by *N*-Bromosuccinimide (*NBS*) in aqueous acetic acid has been studied

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already in several cases[1,2]. The kinetics of oxidation of benzyl alcohol and substituted benzyl alcohols to their aldehydes by *NBS* has also been reported[3,4]. Now we have investigated the kinetics of oxidation of allyl alcohol to acrolein by *NBS* in aqueous medium.

## Experimental

*N*-Bromosuccinimide was prepared by the bromination of succinimide and recrystallised twice[5]. Allyl alcohol, E. Merck, was distilled and used. All solutions were prepared in doubly distilled water. *NBS* was estimated iodometrically. The reaction was carried out in black coated flasks to avoid photochemical reactions, if any. 20 ml each of allyl alcohol, mercuric acetate in aqueous perchloric acid and sodium perchlorate solutions of required concentrations were thermostated at 35 °C. 20 ml of *NBS* solution of the required concentration was added to the mixture after thermostating it for 30 min. The kinetics of the reaction was followed by iodometric estimation of *NBS* in a measured aliquot of the reaction mixture at various time intervals.

*Stoichiometry:* The reaction mixture containing excess of *NBS* over allyl alcohol in presence of $HClO_4$ and $Hg^{+2}$ was kept at 35 °C for 24 h. Estimation of unreacted *NBS* showed that one mol of allyl alcohol consumed one mol of *NBS*. This was found to be the case even without the presence of $Hg^{+2}$. The presence of acrolein was confirmed by spot tests and isolation of its 2,4-dinitrophenyl hydrazone[6].

$$CH_2{=}CH{-}CH_2OH + (CH_2CO)_2NBr \rightarrow CH_2{=}CH{-}CHO + (CH_2CO)_2NH + H^+ + Br^-$$

## Results

The kinetics of oxidation of allyl alcohol by *NBS* was investigated at several initial concentrations of the reactants. When allyl alcohol is in large excess, plots of log (titre) against time are found to be linear with correlation coefficient $> 0.9968$, showing a first order dependence on *NBS*. The pseudo-first order constants in *NBS* ($k'$), calculated at different initial concentrations of the substrate, are found to increase linearly with the increase in allyl alcohol concentration (Table 1). A plot of log $k'$ against log $[\text{allyl alcohol}]_0$ gave a straight line with slope unity, the correlation coefficient $r$ being 0.9965.

When $[NaClO_4]$ was varied from 0 to $0.12\,\text{mol}\,\text{dm}^{-3}$, the pseudo-first order rate constant varied from $8.45 \times 10^{-4}$ to $8.89 \times 10^{-4}\,\text{s}^{-1}$. The rate constant can, therefore, be regarded as independent of the ionic strength of the medium. At higher perchloric acid concentrations, the rate constants remained practically the same but at lower acid concentration, i.e., when $[H^+] < [\text{alcohol}]_0$, the rate constant was considerably larger (Table 2).

It was observed that change in concentration of added mercuric acetate had no effect on the rate (Table 3).

Table 1. *Effect of change in concentration of the reactants on the reaction rate at 35 °C.* [Mercuric Acetate] = 0.005 mol dm$^{-3}$; [H$^+$] = 0.02 mol dm$^{-3}$; [NaClO$_4$] = 0.03 mol dm$^{-3}$

| $[NBS]_0$ mol dm$^{-3}$ | [Allyl alcohol]$_0$ mol dm$^{-3}$ | $10^4 k'$ s$^{-1}$ | $10^2 k_{obs.}$ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| 0.00125 | 0.0200 | 8.26 | — |
| 0.00150 | 0.0200 | 8.44 | — |
| 0.00175 | 0.0200 | 8.65 | — |
| 0.00200 | 0.0200 | 9.11 | — |
| 0.00100 | 0.0200 | 8.48 | 4.24 |
| 0.00100 | 0.0225 | 9.23 | 4.10 |
| 0.00100 | 0.0250 | 10.50 | 4.20 |
| 0.00100 | 0.0275 | 11.67 | 4.24 |
| 0.00100 | 0.0300 | 12.55 | 4.18 |

Table 2. *Effect of* [H$^+$] *on the reaction rate at 35 °C.* [Allyl alcohol]$_0$ = 0.02 mol dm$^{-3}$; $[NBS]_0$ = 0.001 mol dm$^{-3}$; [NaClO$_4$] = 0.03 mol dm$^{-3}$; [Hg$^{+2}$] = 0.005 mol dm$^{-3}$

| [H$^+$] mol dm$^{-3}$ | $10^4 k'$ s$^{-1}$ |
|---|---|
| 0.01 | 12.67 |
| 0.02 | 8.48 |
| 0.03 | 7.78 |
| 0.04 | 7.10 |
| 0.05 | 7.46 |
| 0.06 | 8.05 |

Table 3. *Effect of* [Hg$^{+2}$] *on the reaction rate at 35 °C.* [Allyl alcohol]$_0$ = = 0.02 mol dm$^{-3}$; $[NBS]_0$ = 0.001 mol dm$^{-3}$; [H$^+$] = 0.02 mol dm$^{-3}$; [NaClO$_4$] = 0.03 mol dm$^{-3}$

| [Hg$^{+2}$] mol dm$^{-3}$ | $10^4 k'$ s$^{-1}$ |
|---|---|
| 0 | 13.58 |
| 0.0050 | 8.48 |
| 0.0075 | 8.55 |
| 0.0100 | 8.61 |

To note any possible retardation effect due to the initial addition of one of the products, namely succinimide, the reaction was carried out with different initial concentrations of succinimide. Contrary to the earlier observed retardation[1,7], a slight enhancement in the rate was noticed. The pseudo-first order rate constant changes from $9.18 \times 10^{-4}$ to $10.52 \times 10^{-4}\,s^{-1}$ when the initial concentration of succinimide is varied from $0.01\,mol\,dm^{-3}$ to $0.03\,mol\,dm^{-3}$. The reaction was carried out at three different temperatures, viz. 25°, 35° and 45 °C. The kinetic parameters are as follows:

$E_a = 52.3\,kJ\,mol^{-1}$; $A = 2.009 \times 10^9\,s^{-1}$;
$\Delta S^{\ddagger} = -109.9\,J\,K^{-1}\,mol^{-1}$; $\Delta H^{\ddagger} = 49.7\,kJ\,mol^{-1}$;
$\Delta G^{\ddagger} = 83.6\,kJ\,mol^{-1}$ (at 35 °C).

## Discussion

In the oxidation reactions with *NBS* as the oxidant, in perchloric acid medium, the possible oxidizing species are *NBS*, $Br^+$, HOBr, and $NBSH^+$.

If *NBS* were the oxidizing species the derived rate law should indicate an inverse first order with respect to acid, which is contrary to experimental observations.

Since no retardation effect is noticed, due to the initial addition of succinimide (*S*), $Br^+$ is not likely to be the reactive species.

$$NBSH^+ \rightleftharpoons S + Br^+ \tag{1}$$

The observed slight enhancement in the rate of the reaction, due to the addition of succinimide, also makes HOBr [produced as a result of reactions (2) and (3)], unlikely to be the oxidizing species.

$$Br^+ + H_2O \xrightarrow{\text{fast}} H_2OBr^+ \tag{2}$$

$$H_2OBr^+ \rightleftharpoons HOBr + H^+ \tag{3}$$

Assuming $NBSH^+$ as the oxidizing species, the slight increase in the rate with the addition of succinimide can be explained by equilibrium (1).

Alcohol gets protonated in the acid medium and at higher acid concentrations ($[H^+] > [\text{alcohol}]$), the alcohol may be assumed to exist as protonated alcohol. In *NBS* oxidations it has been proposed that the oxidation involves the removal of an α-hydrogen as hydride ion[2,4]. This will be more difficult in protonated allyl alcohol and hence unprotonated allyl alcohol can undergo oxidation more easily compared to the protonated one. Since the reaction is first order both with *NBS* and alcohol, a mechanism involving the rate determining abstraction of $\alpha$-hydrogen as hydride ion by $NBSH^+$ is proposed and the rate law has been derived accordingly.

$$\underset{(alcH^+)}{CH_2{=}CH{-}CH_2{-}\overset{+}{O}H_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(alc)}{CH_2{=}CH{-}CH_2{-}OH} + H^+;\ \text{fast}$$

$$NBS + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NBSH^+;\ \text{fast}$$

$$CH_2{=}CH{-}CH_2{-}OH + NBSH^+ \xrightarrow{k_3} CH_2{=}CH{-}CHO + S + 2\,H^+ + Br^-;\ \text{slow}$$

Applying the steady state approximation for the reacting species $alc$ and $NBSH^+$ with reasonable approximations, $k_{-1}[H^+] \gg k_3[NBSH^+]$ and $k_{-2} \gg k_3[alc]$, the rate equation becomes

$$-\frac{d[NBS]}{dt} = \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} [NBS][alcH^+]$$

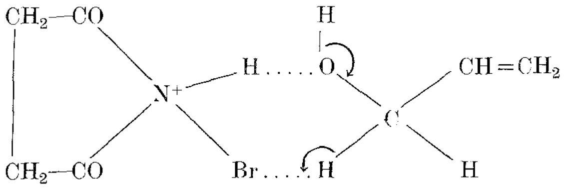
If $[H^+] > [alc]$,
$[alcH^+] = [alc]_T - [alc] \simeq [alc]_T$,

where $[alc]_T$ is the total alcohol concentration. Hence

$$-\frac{d[NBS]}{dt} = \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} [NBS][alc]_T$$

The above rate law explains all the observed facts, viz., first order dependence of reaction rate on the oxidant and the substrate and zero order on the acid when $[H^+] > [alc]$. At lower acid concentration ($[H^+] < [alc]$) unprotonated alcohol concentration will be higher and as a result, an increase in the rate has been experimentally observed. The function of added mercuric acetate is only to trap $Br^-$ formed in the course of the reaction as $HgBr_2$, $HgBr_4^{-2}$ or $Hg(OAc)_2Br_2^{-2}$. At zero $[Hg^{+2}]$ the reaction is probably a mixed oxidation by $NBS$ and $Br_2$.

A highly negative $\Delta S^{\ddagger}$ value suggests a cyclic intermediate.



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