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CONTRASTING KINETIC BEHAVIOUR OF ALLYL AND CROTYL ALCOHOLS TOWARDS *N*-BROMOSUCCINIMIDE IN AQUEOUS METHANOL

C. KARUNAKARAN* AND K. GANAPATHY
Department of Chemistry, Annamalai University, Annamalainagar-608 002, Tamil Nadu, India

The reactions of *N*-bromosuccinimide (NBS) with allyl and crotyl alcohols in aqueous methanol are first order in NBS. Allyl alcohol displays a zero-order dependence whereas crotyl alcohol exhibits a Michaelis–Menten-type dependence on substrate concentration. The NBS–allyl alcohol reaction is inhibited by H^+ whereas the NBS–crotyl alcohol reaction is independent of $[H^+]$. However, both are fast in the absence of acid. The rates are unaffected by the addition of neutral salt and succinimide. The reaction of NBS with crotyl alcohol exhibits a positive dielectric effect whereas allyl alcohol displays no such effect. Inhibition by Hg^{II} is observed in the crotyl alcohol reaction but not with allyl alcohol. 3-Bromo-2-methoxypropan-1-ol is the product of the allyl alcohol reaction but a mixture of 2-bromo-3-methoxybutan-1-ol and 2-bromobutane-1,3-diol in the crotyl alcohol reaction. In the allyl alcohol reaction the formation of solvated bromonium ion and of HOBr is suggested as rate-limiting steps. In the crotyl alcohol reaction, rate determining breakdown of an NBS–crotyl alcohol complex, formed in a fast pre-equilibrium, is proposed.

INTRODUCTION

The kinetics of the bromination[1] and oxidation[2,3] of saturated organic compounds by *N*-bromosuccinimide (NBS) have received considerable attention recently, but there seem to have been no studies of the kinetics of the reaction of NBS with unsaturated alcohols. We have studied the oxidation of allyl alcohol by NBS in aqueous acid medium.[4] It is a second-order reaction, first order with respect to NBS and allyl alcohol. In aqueous methanol the reaction is methoxybromination. This prompted us to investigate the kinetics and mechanism of the reaction of NBS with allyl and crotyl alcohols in aqueous methanol. This paper reports a contrasting kinetic behaviour of the two alcohols under identical conditions, although they react with chloramine-B through a common mechanism.[5]

EXPERIMENTAL

NBS was prepared by the bromination of succinimide and recrystallized. Allyl and crotyl alcohols (Merck) were distilled before use. The reactions were conducted in black-coated flasks to avoid photochemical reactions, if any. The kinetic studies were carried out in aqueous methanol under pseudo-first-order conditions with a large excess of alcohol over NBS. The reactions were followed by iodimetric determination of unreacted NBS. The pseudo-first-order rate constants (k') were calculated from the slopes of linear plots of log titre vs time by the method of least squares. The error quoted in k' is the 95% confidence limit of a Student's t-test. The activation parameters were calculated by the least-squares analysis of Eyring plots.

Product analysis. To the substrate (0·05 mol) in 50% (v/v) aqueous methanol, maintained acidic with perchloric acid, NBS (0·05 mol) was added. Methanol was distilled off under reduced pressure. The product was separated by repeated extraction with diethyl ether and purified by distillation under reduced pressure. ^1H NMR spectroscopy indicated that 3-bromo-2-methoxypropan-1-ol was the product in the allyl alcohol reaction, whereas a mixture of 2-bromo-3-methoxybutan-1-ol and 2-bromobutane-1,3-diol were identified in the crotyl alcohol reaction using ^{13}C NMR spectroscopy and mass spectrometry. Hence the reactions are represented as

$$CH_2{=}CHCH_2OH + (CH_2CO)_2NBr + CH_3OH \rightarrow CH_2BrCH(OCH_3)CH_2OH + (CH_2CO)_2NH$$

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*Author for correspondence.

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and

$$\mathrm{CH_3CH{=}CHCH_2OH + (CH_2CO)_2NBr + HOX}$$
$$\rightarrow \mathrm{CH_3CH(OX)CHBrCH_2OH + (CH_2CO)_2NH}$$

where X = H or CH_3. Owing to the slow decomposition of NBS in aqueous methanol, the stoichiometry of the reactions could not be determined.

RESULTS AND DISCUSSION

The reactions are first order with respect to NBS. Plots of log titre vs time are linear with a correlation coefficient (r) of at least 0·996. The pseudo-first-order rate constant (k') remains constant at different $[\mathrm{NBS}]_0$ (Table 1). The rate of decomposition of the oxidant in the solvent mixture, determined in the absence of substrate, is almost negligible in comparison with the rate of the reactions. The reaction of NBS with allyl alcohol is zero order with respect to the substrate. The pseudo-first-order rate constant remains constant at different $[\text{allyl alcohol}]_0$. The reaction with crotyl alcohol, in dramatic contrast, displays a Michaelis–Menten type of behaviour with respect to the substrate. The double reciprocal plot of k' vs. $[\text{crotyl alcohol}]_0$ is linear with a definite y-intercept ($r = 0{\cdot}9998$). The reactions of NBS with other β,γ-unsaturated alcohols such as cinnamyl alcohol are fast under identical conditions.

The reactions display a novel acid dependence. At constant ionic strength (μ), maintained with sodium perchlorate, the rate of the NBS–allyl alcohol reaction decreases with increase in $[\mathrm{H^+}]$ whereas the NBS–crotyl alcohol reaction exhibits no dependence on $[\mathrm{H^+}]$, where $[\mathrm{H^+}]$ is calculated from pH measurements. In the absence of acid both the reactions are fast (Table 2).

Variation of the ionic strength of the medium and addition of succinimide have negligible influences on the rates of the reactions. Initial addition of acrylonitrile to the reaction mixtures neither induces polymerization nor retards the reactions, indicating the absence of any free-radical intermediate. Under the experimental conditions, there is no reaction between NBS and acrylonitrile. The rate data at different solvent compositions (Table 3) show that the reaction of NBS with allyl alcohol is independent of solvent polarity whereas that with crotyl alcohol exhibits a positive dielectric effect. An increase in the methanol content of the solvent, at a constant concentration of perchloric acid, leads to a small increase in the pH of the medium. As the NBS–allyl alcohol reaction is inhibited by hydrogen ion, it may be assumed that the decrease in rate due to hydrogen ion inhibition is approximately compensated by a small positive dielectric effect.

Table 1. Pseudo-first-order rate constants for the reactions of NBS with allyl and crotyl alcohols in 50% (v/v) aqueous methanol at 35 °C[a]

$10^3[\mathrm{NBS}]_0$/ mol dm^{-3}	$10^2[\mathrm{alc}]_0$/ mol dm^{-3}	$10^4k'/\mathrm{s^{-1}}$	
		Allyl alcohol	Crotyl alcohol
1·0	2·0	7·19 ± 0·47	27·9 ± 2·9
1·5	2·0	5·69 ± 0·29	25·4 ± 1·5
2·5	2·0	5·89 ± 0·48	27·1 ± 1·7
3·0	2·0	5·85 ± 0·36	27·9 ± 2·1
2·0	1·0	5·76 ± 0·72	17·7 ± 0·6
2·0	2·0	6·23 ± 0·52	30·7 ± 1·3
2·0	3·0	6·24 ± 0·34	42·6 ± 2·2
2·0	4·0	5·88 ± 0·37	50·3 ± 1·9
2·0	5·0	5·71 ± 0·35	57·7 ± 5·0
2·0	6·0	6·03 ± 0·55	—

[a] $[\mathrm{H^+}] = 0{\cdot}0123$ mol dm^{-3}; $\mu = 0{\cdot}06$ mol dm^{-3}.

Table 2. Dependence of the rates on $[\mathrm{H^+}]$ at 35 °C[a]

$10^2[\mathrm{H^+}]$/mol dm^{-3}	$10^4k'/\mathrm{s^{-1}}$	
	Allyl alcohol	Crotyl alcohol
0·00	Fast	Fast
0·28	12·5 ± 1·2	—
0·68	11·5 ± 0·7	28·3 ± 1·6
1·00	6·77 ± 0·47	—
1·23	6·23 ± 0·52	30·7 ± 1·3
1·86	4·73 ± 0·42	28·4 ± 1·2
2·34	4·73 ± 0·49	25·6 ± 1·5
2·82	4·30 ± 0·47	30·4 ± 0·6
3·39	4·13 ± 0·29	27·7 ± 1·7

[a] $[\mathrm{NBS}]_0 = 0{\cdot}002$ mol dm^{-3}; $[\mathrm{alc}]_0 = 0{\cdot}02$ mol dm^{-3}; $\mu = 0{\cdot}06$ mol dm^{-3}; solvent = 50% (v/v) MeOH–H_2O.

Mercury(II) acetate has no effect on the rate of the reaction of NBS with allyl alcohol whereas the crotyl alcohol reaction is inhibited by $\mathrm{Hg^{II}}$ – a feature that is completely different from that observed in the reaction of NBS with saturated alcohols (Table 4). The activation parameters were calculated from rate measurements at 25, 35 and 45 °C using Eyring plots (Table 5).

Table 3. Effect of solvent composition on the rates at 35 °C[a]

MeOH–H_2O (%, v/v)	$10^2[\mathrm{H^+}]$/ mol dm^{-3}	$10^4k'/\mathrm{s^{-1}}$	
		Allyl alcohol	Crotyl alcohol
70:30	1·07	6·59 ± 0·28	10·0 ± 0·5
60:40	1·12	6·17 ± 0·25	18·1 ± 1·3
50:50	1·23	6·23 ± 0·52	30·7 ± 1·3
40:60	1·38	5·64 ± 0·29	50·7 ± 1·7
30:70	1·55	6·77 ± 0·18	90·6 ± 4·1
0:100	2·00	13·6[b]	Fast

[a] $[\mathrm{NBS}]_0 = 0{\cdot}002$ mol dm^{-3}; $[\mathrm{alc}]_0 = 0{\cdot}02$ mol dm^{-3}; $\mu = 0{\cdot}06$ mol dm^{-3}.

[b] $[\mathrm{NBS}]_0 = 0{\cdot}001$ mol dm^{-3}; $\mu = 0{\cdot}05$ mol dm^{-3}; product and kinetic order are different.[4]

Table 4. Effect of $[\mathrm{Hg^{II}}]$ on the rates at 35 °C[a]

	$10^4k'/\mathrm{s^{-1}}$	
$10^3[\mathrm{Hg^{II}}]/\mathrm{mol\ dm^{-3}}$	Allyl alcohol	Crotyl alcohol
0	6·23 ± 0·52	30·7 ± 1·3
4	5·54 ± 0·67	20·5 ± 1·2
5	5·86 ± 0·35	19·9 ± 0·5
6	5·53 ± 0·78	20·3 ± 1·7

[a] $[\mathrm{NBS}]_0 = 0{\cdot}002\ \mathrm{mol\,dm^{-3}}$; $[\mathrm{alc}]_0 = 0{\cdot}02\ \mathrm{mol\,dm^{-3}}$; $[\mathrm{H^+}] = 0{\cdot}0123\ \mathrm{mol\,dm^{-3}}$; $\mu = 0.06\ \mathrm{mol\,dm^{-3}}$; solvent = 50% (v/v) $\mathrm{MeOH{-}H_2O}$.

Table 5. Activation parameters of the reactions of NBS with allyl and crotyl alcohols in 50% (v/v) aqueous methanol[a]

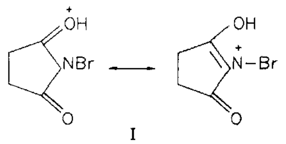
Substrate	$\Delta H^{\neq}/$ kJ mol^{-1}	$-\Delta S^{\neq}/$ J K^{-1}mol^{-1}	$\Delta G^{\neq\,b}/$ kJ mol^{-1}
Allyl alcohol	73·2	69·2	94·5
Crotyl alcohol	47·9	138	90·4

[a] $[\mathrm{NBS}]_0 = 0{\cdot}002\ \mathrm{mol\,dm^{-3}}$; $[\mathrm{alc}]_0 = 0{\cdot}02\ \mathrm{mol\,dm^{-3}}$; $[\mathrm{H^+}] = 0{\cdot}0123\ \mathrm{mol\,dm^{-3}}$; $\mu = 0{\cdot}06\ \mathrm{mol\,dm^{-3}}$.
[b] at 35 °C.

Mechanism and rate law

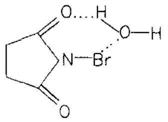
NBS–allyl alcohol reaction

The possible reactive species of NBS in acidic medium are molecular NBS, protonated NBS ($\mathrm{NBSH^+}$), HOBr and solvated bromonium ion.[2–4] In NBS brominations or oxidations of organic substrates, it is generally proposed that the molecular NBS acts only through the positive halogen end.[3] As the reaction is zero order with respect to substrate, molecular NBS is unlikely to be the reactive species. Most investigators have assumed the protonation of NBS in acidic medium with the proton bonded at nitrogen.[2,6] In amides protonation at oxygen has been reported.[7] In imides, owing to the decreased electron density at nitrogen, protonation is more likely at the carbonyl oxygen. Hence the most probable structure of $\mathrm{NBSH^+}$ is one with the proton bonded at oxygen rather than nitrogen (I).



I

However, the reaction is inhibited by hydrogen ion, and hence $\mathrm{NBSH^+}$ is not considered to be the reactive species. Solvated bromonium ion is likely to be reactive. To account for the novel acid dependence, HOBr formed by the hydrolysis of NBS, which is an aqueous medium owing to its positive bromine end, is likely to be associated with one water molecule (II), is also considered as a reactive species. As the reaction is zero order with respect to allyl alcohol, formation of solvated bromonium ion (Scheme 1) and HOBr (Scheme 2) are supposed to be slow and rate-limiting.



II

$$\mathrm{(CH_2CO)_2NBr} \xrightarrow[\text{slow}]{k_1} \mathrm{(CH_2CO)_2N^-} + \mathrm{Br^+}$$

$$\mathrm{Br^+} + \text{alcohol} \longrightarrow \text{product}$$

$$\mathrm{(CH_2CO)_2N^-} + \mathrm{H^+} \longrightarrow \mathrm{(CH_2CO)_2NH}$$

Scheme 1

$$\mathrm{II} + \mathrm{H_2O} \overset{K_2}{\rightleftharpoons} \mathrm{(CH_2CO)_2N{-}Br\cdots\bar{O}{-}H} + \mathrm{H_3O^+} +$$

$$\mathrm{(CH_2CO)_2N{-}Br\cdots\bar{O}{-}H} \xrightarrow[\text{slow}]{k_3}$$

$$\mathrm{(CH_2CO)_2N^-} + \mathrm{HOBr}$$

$$\mathrm{HOBr} + \text{alcohol} \longrightarrow \text{product}$$

$$\mathrm{(CH_2CO)_2N^-} + \mathrm{H^+} \longrightarrow \mathrm{(CH_2CO)_2NH}$$

Scheme 2

The above equilibria and reactions lead to the rate law

$$-\mathrm{d}[\mathrm{NBS}]/\mathrm{d}t = (k_1 + K_2k_3/[\mathrm{H^+}])[\mathrm{NBS}] \qquad (1)$$

The pseudo-first-order rate constant being

$$k' = k_1 + K_2k_3/[\mathrm{H^+}] \qquad (2)$$

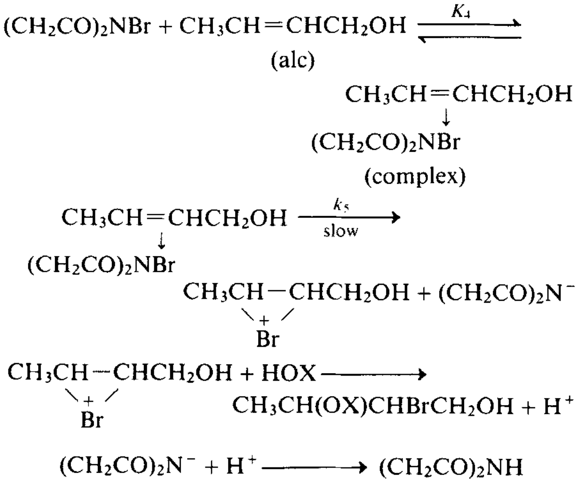
A linear plot of k' vs $1/[\mathrm{H^+}]$ ($r = 0{\cdot}898$) confirms the applicability of rate law (1). Even though protonation of NBS should facilitate the release of $\mathrm{Br^+}$, formation of $\mathrm{Br^+}$ through $\mathrm{NBSH^+}$is not considered as the $\mathrm{NBS{-}HClO_4}$ pH titration curve shows no appreciable protonation. Another simple route for HOBr formation is

$$\mathrm{(CH_2CO)_2NBr} + \mathrm{OH^-} \xrightarrow{k^*} \mathrm{HOBr} + \mathrm{(CH_2CO)_2N^-}$$

This is in accordance with the experimental findings. The term K_2k_3 may be replaced by the term k^*K_w, where K_w is the ionic product of water. However, this route is unlikely as the reaction has been conducted in acidic medium.

NBS–crotyl alcohol reaction

The reaction exhibits Michaelis–Menten kinetics, suggesting the formation of a complex between the reactive species and the substrate. If $\mathrm{NBSH^+}$ were to be the active species, contrary to the experimental observation, the rate law should predict a first-order dependence on $[H^+]$. The reaction is not retarded by succinimide, and hence HOBr and solvated bromonium ion are less likely to complex with the substrate. A positive dielectric effect and the absence of a primary salt effect suggest a dipole–dipole interaction leading to a polar transition state. Hence molecular NBS is considered to be the reactive species and formation of a molecular NBS–crotyl alcohol complex in a fast pre-equilibrium followed by its slow breakdown is proposed as the reaction mechanism (Scheme 3). To account for the fact that the reaction is fast in the absence of acid, HOBr formed by the rate-limiting hydrolysis of molecular NBS is also considered as a reactive species and is assumed to react with the substrate in a fast step (Scheme 2).



$$(CH_2CO)_2NBr + \underset{\text{(alc)}}{CH_3CH{=}CHCH_2OH} \xrightleftharpoons{K_4} \underset{\text{(complex)}}{\begin{array}{c}CH_3CH{=}CHCH_2OH\\ \downarrow\\ (CH_2CO)_2NBr\end{array}}$$

$$\begin{array}{c}CH_3CH{=}CHCH_2OH\\ \downarrow\\ (CH_2CO)_2NBr\end{array} \xrightarrow[\text{slow}]{k_5} \begin{array}{c}CH_3CH{-}CHCH_2OH\\ \diagdown_{+}\diagup\\ Br\end{array} + (CH_2CO)_2N^-$$

$$\begin{array}{c}CH_3CH{-}CHCH_2OH\\ \diagdown_{+}\diagup\\ Br\end{array} + HOX \longrightarrow CH_3CH(OX)CHBrCH_2OH + H^+$$

$$(CH_2CO)_2N^- + H^+ \longrightarrow (CH_2CO)_2NH$$

where X = H or CH_3

Scheme 3

The rate law for the proposed mechanism (Schemes 2 and 3) is derived as

$$-d[NBS]_T/dt = \frac{(K_4k_5[alc] + K_2k_3/[H^+])[NBS]_T}{1 + K_4[alc]} \tag{3}$$

where $[NBS]_T = [NBS] + [complex]$. The pseudo-first-order rate constant is

$$k' = \frac{K_4k_5[alc] + K_2k_3/[H^+]}{1 + K_4[alc]} \tag{4}$$

In acidic medium, the rate of formation of HOBr, traced from the kinetic study of the NBS–allyl alcohol reaction under identical conditions, is lower than that of the rate of the NBS–crotyl alcohol reaction. It is likely to be suppressed further owing to the complexation of NBS with crotyl alcohol. Hence, assuming $K_2k_3/[H^+] \ll K_4k_5[alc]$, the pseudo-first-order rate constant simplifies to

$$k' = K_4k_5[alc]/(1 + K_4[alc]) \tag{5}$$

From the slope–intercept relationship, the equilibrium and rate constants at 35 °C have been calculated as $k_1 = 3{\cdot}97 \times 10^{-4}\ s^{-1}$, $K_2k_3 = 2{\cdot}73 \times 10^{-6}\ mol\,dm^{-3}\,s^{-1}$, $K_4 = 15{\cdot}4\ dm^3\,mol^{-1}$ and $k_5 = 1{\cdot}33 \times 10^{-2}\ s^{-1}$.

In the absence of acid, the term $K_2k_3/[H^+]$ in rate laws (1) and (3) becomes large and hence accounts for the fast reactions. Complex formation between NBS and crotyl alcohol is also observed in aqueous ethanol under identical conditions. The reaction rate is almost the same as that in aqueous methanol, and the equilibrium constant (K_4) and the rate constant (k_5) are measured as $8{\cdot}73\ dm^3\,mol^{-1}$ and $1{\cdot}90 \times 10^{-2}\ s^{-1}$, respectively. The thermodynamic parameters of the reaction in aqueous ethanol ($\Delta H^{\neq} = 49.3\ kJ\,mol^{-1}$; $\Delta S^{\neq} = -133\ J\,K^{-1}\,mol^{-1}$ and $\Delta G^{\neq} = 90{\cdot}4\ kJ\,mol^{-1}$) are in close agreement with those in aqueous methanol. The function of Hg^{II} is generally to trap Br^-, formed as a consequence of oxidation of the substrate, as either non-ionized $HgBr_2$ or more likely as $HgBr_4^{2-}$.[6] Hg^{II} also plays a catalytic role through the formation of an NBS–Hg^{II} complex.[8] The inhibition by Hg^{II} of the NBS reaction with crotyl alcohol but not that with allyl alcohol is probably due to the complex formation between Hg^{II} and allyl and crotyl alcohols.[9] A possible explanation for the contrasting kinetic behaviour of the two alcohols towards the same reagent, in a high-dielectric medium, under identical conditions, is that crotyl alcohol with a rich electron density at the olefinic linkage, due to the $+I$ effect of methyl group, complexes with the oxidant itself in fast pre-equilibrium whereas allyl alcohol reacts with active species derived from the oxidant.

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