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Kinetics and Mechanism of Oxidation of 2-Oxopropionic Acid by N-Bromosaccharin in Aqueous Acetic Acid Medium

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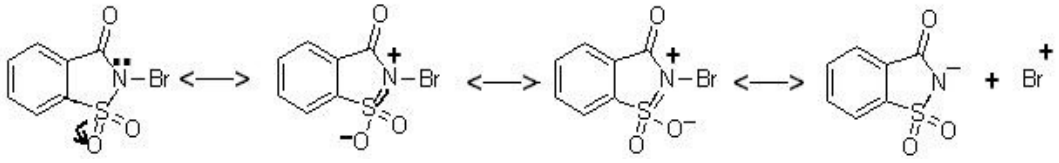
Abstract

In an acidic media with a temperature range of 313-325K, the kinetics of 2-oxopropionic acid oxidation by N-bromosaccharin in aqueous acetic acid medium were investigated. In the case of [2-oxopropionic acid], the reaction was revealed to be first order. [H^+] has also been observed to provide an effect. The velocity of reaction rises somewhat as the ionic strength of the medium increases. In the oxidation process, a 1:1 stoichiometry is found. A convincing mechanism has been presented based on the experimental data. All of the experimental data may be explained by a rate equation derived from this process. The Arrhenius equation is derived from the influence of temperature on reaction rate.

Key words: Kinetics investigation, N-bromosaccharin, 2-oxopropionic acid, ionic strength, mechanism

INTRODUCTION

N-bromosaccharin is an imide of orthosulphobezenoic acid that is more potent than other di-carboxylic acid imides like succinic acid. Saccharin's anion receives additional long - term stability from of the acyl and sulphonyl groups, that provide a larger orbital for electron delocalization[1,2] and has been satisfactorily used as an oxidant for the oxidation of benzaldehyde and substituted benzaldehydes[3], propiophenone and butyrophenone[4], mandelic acid and substituted madelic acids[5,6], glycolic acid and lactic acid[7,8], Benzhydrol and substituted benzhydrols[9], benzyl alcohol[10], secondary alcohols[11], cyclohexanol and tert-butyl cyclohexanols[12-14], thiols[15], selenanones[16,] oximes[17]etc.



The 2-oxopropionic acid has a wide range of biological applications and is an important component of pharmaceutical chemistry. The 2-oxopropionic acid and its derivatives, for example, are antirheumatic agents in humans. It has a significant impact on the suppression of adjuvant arthritis[18-23]. For the first

time, the kinetics and mechanistic route of 2-oxopropionic acid oxidation by NBSA (oxidant) were investigated.

EXPERIMENTAL

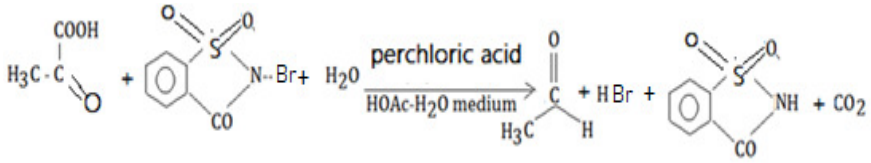
N-bromosaccharin (Aldrich sample) was utilised as an oxidant. The literature methodology was used to purify acetic acid (A. R. grade). In an acetic acid-water mixture, a standard solution of 2-oxopropionic acid (substrate) (A. R. grade) was created. In all kinetic runs, double distilled water has been used. The freshly created solution of N-bromosaccharin was kept in an amber coloured bottle to avoid photochemical effects, and its strength was estimated iodometrically[24] using a 1 percent solution of freshly prepared starch as an indicator.

Kinetic measurements

By maintaining a large excess of 2-oxopropionic acid (substrate) over oxidant N-bromosaccharin, all kinetic experiments were conducted under pseudo first-order conditions. At 313 K, mixtures containing the required volumes of N-bromosaccharin solutions in 30% acetic acid were allowed to equilibrate. A determined amount of pre-equilibrated standard solution of N-bromosaccharin was added to this mixture. The reaction mixture was maintained in a thermostat water bath to maintain the desired temperature (within 0.1°C), and the progress of the reaction was monitored iodometrically24 by withdrawing aliquots of the reaction mixture at regular intervals of time. From a linear least squares plot of log [a – x] versus time, the pseudo first order rate constants k' were computed. The rate constants were found to be repeatable to within 5% in duplicate kinetic runs.

Product analysis and stoichiometry

According on this stoichiometric data, it can be deduced that for entire oxidation, the predicted mole ratio of [NBSA] and [substrate] reveals that one mole of each substrate consumes one mole of oxidant. Thus, experimentally, stoichiometric equations can be expressed as:



The melting points of the 2, 4-dinitrophenylhydrazone (2,4-DNP) derivative of the oxidation products as indicated verified with their after original samples of substrate were determined, and the acetaldehyde[25,26] were identified as end-products for 2-oxopropionic acid, respectively.

Substrate	Main oxidation Product	Melting points of 2,4-DNP Derivatives of oxidation products	
		Observed mp ^{0}C	Literature mp ^{0}C
2-oxopropionic acid	Acetaldehyde	167.9 ^{0}C	165-168 °C (lit.)

Table: **1**

Summary: Dependence of rate of oxidation reaction on the initial concentration of oxidant

[PA]	=	$1.25X10^{-2}$ (mol.dm.$^{-3}$)
[H^+]	=	$1.25X10^{-3}$ (mol.dm.$^{-3}$)
HOAc-H_2O	=	30%(v/v),
Temperature	=	313 K.

RESULTS AND DISCUSSION

Under pseudo first-order conditions, the kinetics of NBSA oxidation of 2-oxopropionic acid (substrate) in 30% acetic acid was studied at 313 K. The slopes of such plots were evaluated with regard to the [NBSA], and the plot of log (a-x) vs. time was discovered to be linear, suggesting first order dependency on the reaction rate (Table: 2).**Table: 2**

It was observed that the rate constant (k') increased with increasing substrate concentrations, but that it tended to 1 to 0 order, and that the plot of 1/k' vs 1/ [2-oxopropionic acid] was linear (r2 = 0.9939) with slope less than unity for both substrates, indicating a fractional order (n = 0.47) dependence on rate of [2-oxopropionic acid] (Fig.1). The process is fully catalyzed by perchloric acid, however the rate of the reaction increases as the concentration of [H+] ions rises. The plots of k1 vs. [H+] and log k1 vs. log

[NBSA]10^3 (mol.dm.$^{-3}$)	2-oxopropionic acid (PA)
	$10^4k_1(s^{-1})$
1.00	1.07
1.25	1.09
2.00	1.06
2.50	1.07
4.00	1.06
5.00	1.06

[H+] are both linear with a positive unit slope, indicating that the reaction is completely catalysed. (See Figure 2).

The velocity of reaction was slowed by varying the additional amounts of saccharin, which is one of the oxidation products. Because of the inertness of free radicals, the reaction neither induces polymerization nor slows down the rate of reaction. By varying the concentration of acetic acid from 20 to 60%, the influence of solvent composition on reaction rate was investigated. According to the rate constants, the rate of reaction rises somewhat as the acetic acid concentration of the solvent combination increases.

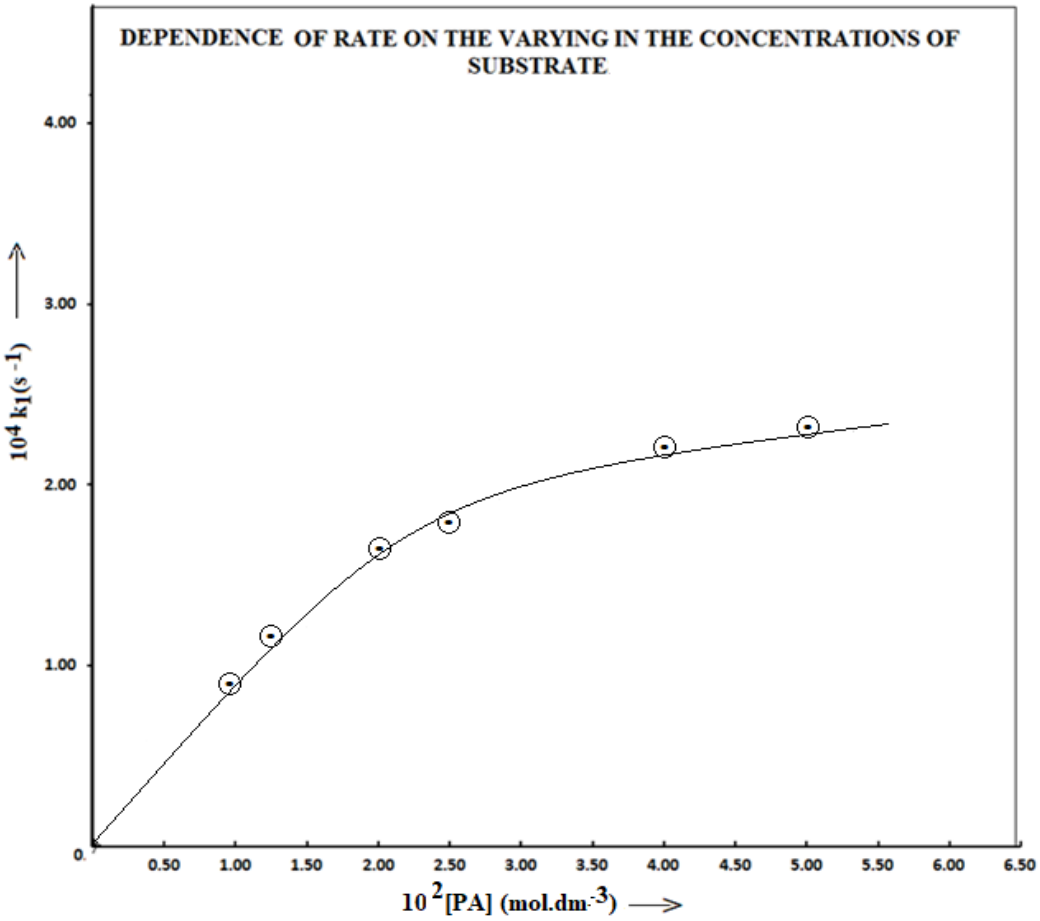
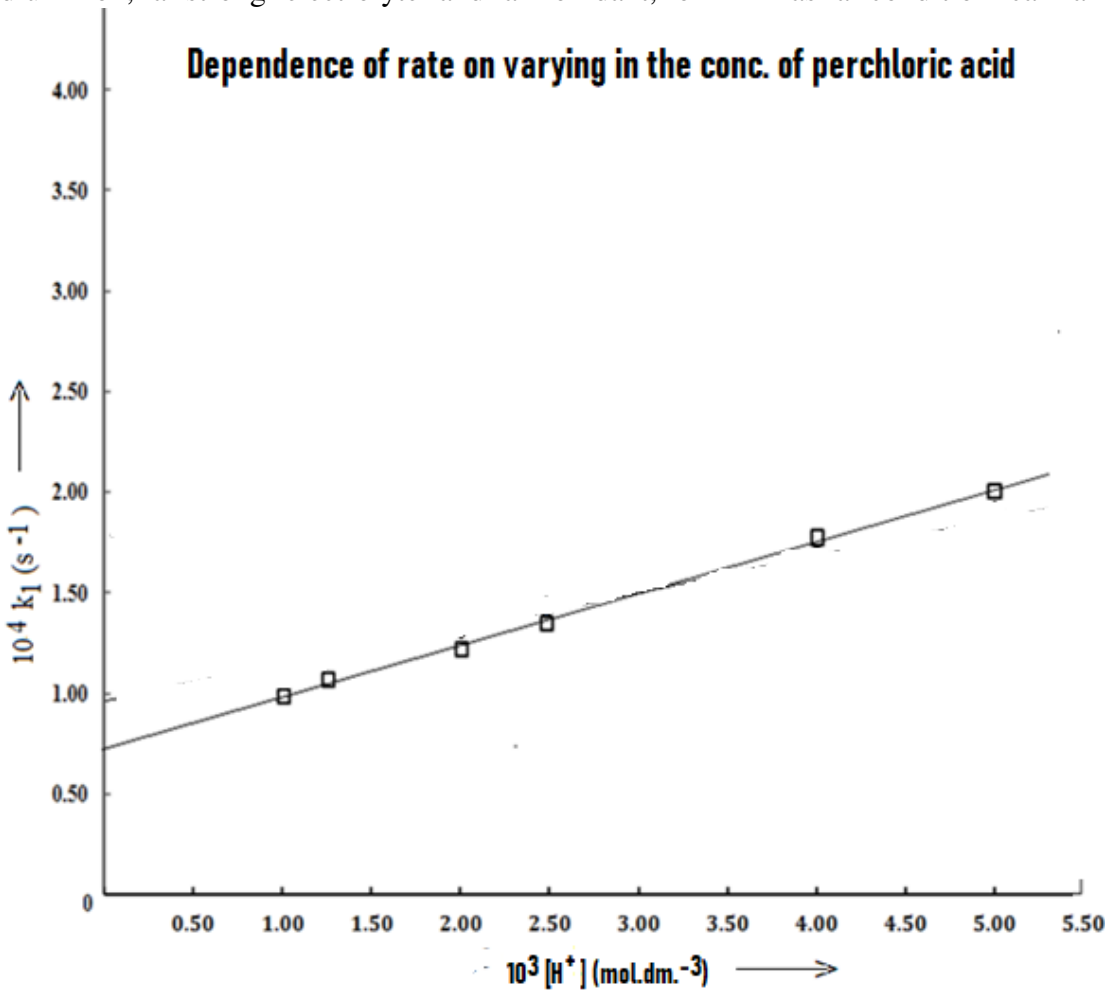


Fig.1: Dependence of rate on the varying in the concentrations of substrate

[NBSA]	=	$2.50X10^{-3}$ (mol.dm.$^{-3}$)
$[H^+]$	=	$1.25X10^{-3}$ (mol.dm.$^{-3}$)
HOAc-H_2O	=	30%(v/V),
Temperature	=	313 K.

REACTIVE SPECIES OF OXIDANT

Before delving into the mechanism of the oxidation process, it's important considering how to slow down the reactive species of NBSA in an aqueous acetic acid media. There is a chance that electrophilic species in aqueous acetic acid are free ions, according to the literature. The molecular NBSA or its hydrolytic product HOBr has been reported as an active species in aqueous acetic acid media. In the presence of an H^+ ion, NBSA or another N-halo oxidant may form a protonated species, $NBSAH^+$, H_2O^+Br hypobromus acidium ion, a strong electrolyte and an oxidant, or Br+ as a condition can affect species[1-14].



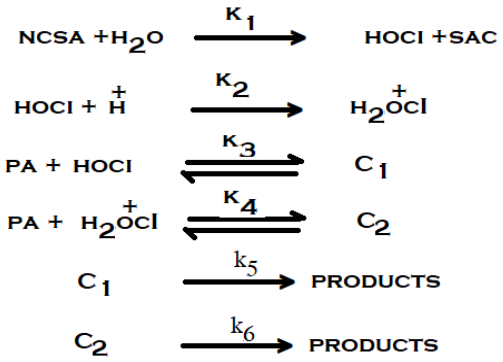
[NBSA]	=	$2.50X10^{-3}$ (mol.dm.$^{-3}$)
[PA.]	=	$1.25X10^{-2}$ (mol.dm.$^{-3}$)
HOAc-H_2O	=	30%(v/V),
Temperature	=	318 K.

Fig.2: Dependence of rate on the varying in the concentrations of perchloric acid

Premised on kinetic data, the generation of reacting species may be explained. With the addition of saccharin to the reaction mixture, the reaction rate was slowed, indicating that the pre-equilibrium stage involves a process in which saccharin is one of the products. This excludes the probability of NBSA and $NBSAH^+$ becoming the reacting species. The massive negative reaction constant indicates a high cationic centre, and the medium's high dielectric constant suggests that H_2O^+Br might be a reactive species.

MECHANISM

In view of the above experimental kinetic data, facts and finding, a suitable mechanism has been proposed for the oxidation of 2-oxopropionic acid (Pyruvic acid) – NBSA system as:



Where**, PA** is standing for 2-oxopropionic acid (Pyruvic acid)

Rate law: The rate law derived for the above mechanism is:

$$k_{obs.} = \frac{K_1\,[PA]\,\{K_3k_5 + K_2K_4k_6\}[H^+]}{[Sac] + K_1(1 + K_3[PA])}$$

As a result, the rate equation above explains all of the experimental kinetics facts and outcomes. At various temperatures, the rate of oxidation was calculated, and the Arrhenius plots of log k vs 1/T were all linear (Fig. 3). The activation and thermodynamic parameters for the scheme's equilibrium and rate-determining steps were calculated using these graphs (Table:3).**Table: 3**

Thermodynamics parameters

Substrate	**Ea** KJ mol^{-1}	**A** s^{-1}	$\Delta H^{\#}$ KJ mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}	$\Delta S^{\#}$ JK^{-1} mol^{-1}
Pyruvic acid	46.80 ±0.81	$1.17x10^3$ ±0.86	48.56 ±0.97	-73.182 ±0.99	-94.39 ±0.87

The S# values that were observed are huge and negative. It's possible to deduce that the percentage of collisions becomes more stringent, and activation complex breakdown is a slow process. The symbol H# signifies enthalpy-controlled reactions.

Furthermore, the consistency of the computed G# values for this oxidation reaction suggests that the same type of reaction mechanism may be at work.

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