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KINETICS OF OXIDATION OF BENZOIN BY N-BROMOSUCCINIMIDE

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ABSTRACT

Kinetics of Oxidation of benzoin by N-bromosuccinimide [NBS] 80% aqueous acetic acid has been investigated. The reaction follows first-order kinetics with respect to both [NBS] and [benzoin]. The effect of varying ionic strength and dielectric constant indicate the reaction is dipole-dipole type. Addition of succinimide (>NH), has a retarding effect on the rate of oxidation. The product of oxidation is benzil. By studying the effect of temperature on the reaction rate, the Arrhenius and the activation parameters have been calculated. A suitable mechanism has been proposed and a rate law explaining the experimental results is derived.

Introduction

Kinetics investigations involving esters,[1] alcohols,[2,3] ketones[4,5] and aminoacids[6] by NBS as oxidizing agent have been reported. We report herein the oxidation of benzoin with NBS in 80% aqueous acetic acid medium.

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Materials and Methods

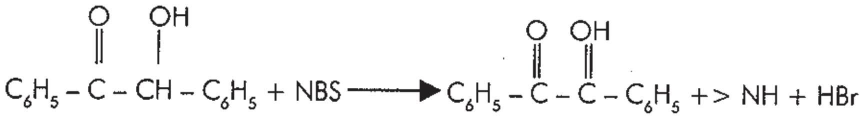
N-bromosuccinimide (GR,S. Merck) was used and its solution was always prepared fresh and its strength was checked by iodometric method. Analar BDH sample of benzoin was used. Sodium nitrate, perchloric acid, and sodium bromide used were of analar grade. Triply distilled water was used throughout the course of investigation. Glacial acetic acid (A.R.Qualigen) was purified and 80% of acetic acid 20% water mixture was used.

Kinetic Measurements

Rate studies were carried out at a constant temperature. All solutions were thermostated for 30 minutes before mixing. Requisite amounts of benzoin, sodium nitrate and aqueous acetic acid were taken in jena glass reaction vessel and placed in a water thermostat maintained at the desired temperature. Reaction was initiated by the rapid addition of NBS solution and its progress followed by estimating iodometrically the amount of unconsumed NBS at regular intervals of time.

Stoichiometry and Product Analysis

Stoichiometric study: N-bromosuccinimide concentration was taken in excess than the concentration of benzoin. It was found that one mole of benzoin reacted with one mole of N-bromosuccinimide to form the products.



$$C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{|}}{CH}-C_6H_5+NBS\longrightarrow C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{OH}{\|}}{C}-C_6H_5+{>}NH+HBr$$

Product study: The concentration of benzoin was taken in excess when compared to the concentration of N-bromosuccinimide and these two were mixed in 80% acetic acid and kept in a hot water bath (kept at 50°C) for about 3 to 6 hours. After that it was cooled and the unreacted NBS was neutralized using thio and the contents were poured in about 100 ml water and this was shaken well. Solvent ether was added and stirred well and poured in a separating funnel. The upper layer (ether layer) was collected after washing several times with water, dried and the product was analysed. TLC confirmed the presence of benzil.

Results and Discussion

Effect of Varying [Oxidant]:

The kinetics were studied at several initial [NBS] keeping other variable parameters constant. Under the condition of [NBS] << [Benzoin] the plots of log[NBS] vs time was linear (r = 0.987) indicating first-order dependence on [NBS].

Effect of Varying [Reductant]:

Investigations were carried out at different initial concentrations of benzoin, keeping other parameters constant (Table 1). The plot of log k_{obs} vs log[Benzoin] was also linear (r = 0.999) with unit slope showing first-order dependence on [Benzoin].

Table 1. Effect of [benzoin] and [$NaNO_3$] on the NBS oxidation of benzoin in aqueous acetic acid medium.

Solvent = 80% ACOH Temperature = 308 K

[NBS] x 10^3 mol dm^{-3}	[Benzoin] x 10^3 mol dm^{-3}	[$NaNO_3$] mol dm^{-3}	k_{obs} x 10^4 s^{-1}
2.00	1.00	0.10	1.28
2.00	2.00	0.10	2.47
2.00	3.00	0.10	3.84
2.00	4.00	0.10	4.97
2.00	2.00	0.05	2.09
2.00	2.00	0.10	2.47
2.00	2.00	0.15	3.32
2.00	2.00	0.20	4.54

Effect of Varying [Percholoric acid] and [Sodium Bromide]

Effect of [H^+] was investigated by varying [$HClO_4$]. Increase of [H^+] ion decreased the rate constant of reaction. Addition of [NaBr] had no effect on the rate of oxidation.

Effect of Varying Ionic Strength

Addition of [$NaNO_3$] to the reaction mixture increased the rate of the reaction (Table-1). The plot of log k_{obs} vs μ was linear (r = 0.974) with positive slope, indicates that the reaction is between two-dipoles.

Effect of Dielectric Constant:

In order to determine the rate dependence on solvent composition, kinetics were followed in 80% glacial acetic acid-water mixtures in which ratio of water to acetic acid was varied. It was observed that on increasing the dielectric constant of the medium increased the rate constant. Plot of log k_{obs} vs 1/D where D is dielectric constant of the medium, was linear (r = 0.929) with negative slope, indicating the reaction is a dipole-dipole type.

Effect of Added [Succinimide]:

Effect of added succinimide [>NH] was studied at different initial concentration of succinimide. It was found that rate of the reaction decreased on increasing [>NH]. Thus added succinimide has a retarding effect on the rate of oxidation. Further, the plot of $1/k_{obs}$ vs [>NH] was linear (r = 0.910) indicating inverse dependence of rate on [>NH][8].

Effect of temperature:

The oxidation of benzoin was studied at different temperatures (308-324 K), the Arrhenius and the activation parameters were evaluated (Table-2). Arrhenius plot of log k_2 vs 1/T was linear (r = 0.936). The energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), free energy of activation ($\Delta G^{\#}$) and pre-exponential factor (A) were found to be 51.67 kJ mol^{-1}, 49.09 kJ mol^{-1}, - 114.14 J K^{-1} mol^{-1}, 16.50 kJ mol^{-1} and 7.0×10^{6} dm^3 mol^{-1} s^{-1} at 308 K respectively.

Table 2. Effect of temperature on the rate of reaction

$[NBS] = 2 \times 10^{-3}$ mol dm^{-3}
$[benzoin] = 2 \times 10^{-2}$ mol dm^{-3}
$[NaNO_3] = 0.1$ mol dm^{-3}
Solvent = 80% aq. ACOH

Temp K	$k_1 \times 10^4$ s^{-1}	$k_2 \times 10^2$ dm^3 mol^{-1} s^{-1}
308	2.47	1.23
313	2.63	1.32
318	4.06	2.03
324	6.40	3.20

Mechanism

Assuming HOBr[8] is the effective oxidising species in the present investigation, the following mechanism is proposed.

$[NBS] + H_2O \overset{k_1}{\rightleftharpoons} [>NH] + [HOBr]$ .... (fast) (1)

$[Benzoin] + [HOBr] \overset{k_2}{\rightleftharpoons}$ Complex .... (fast) (2)

Complex $\xrightarrow{k_3}$ Product .... (slow) (3)

Rate $= k_3$ [complex]. (4)

Using equilibrium approximation for equations (1) and (2)

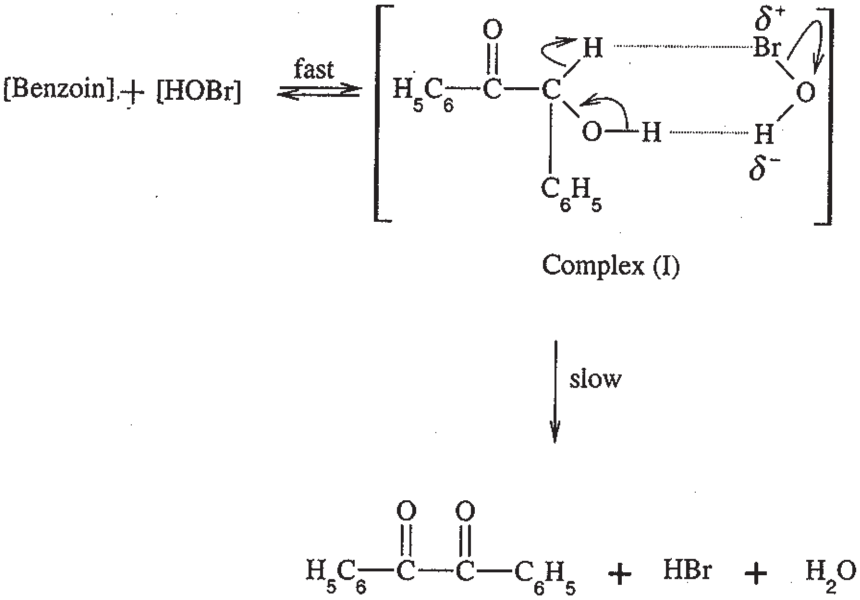
$$k_1 = \frac{[>NH][HOBr]}{[NBS]} \qquad (5)$$

$$k_2 = \frac{[Complex]}{[Benzoin][HOBr]} \qquad (6)$$

Using equation (5) and (6), equation (4) becomes

$$\text{Rate}=\frac{k_1k_2k_3\,[\text{Benzoin}][\text{NBS}]}{[>\text{NH}]}$$

The rate-law predicts the first-order dependence on [Benzoin] and [NBS]. This also explains the retardation in rate on [succinimide]. Increase in rate by the increase of ionic strength of medium may be explained by the polar nature of the intermediate. The effect of dielectric constant indicates the reaction is a dipole-dipole type. Decrease of rate of the reaction by addition of [H^+] ion is explained by its formation in the slow-step (3). The negative $S^{\#}$ value may be explained due to the formation cyclic intermediate[6,9](I).



Complex (I)

Conclusion

The oxidation of benzoin with NBS was found to be first-order with respect to [NBS] and [benzoin]. Increases of [H^+] decreased the rate of reaction. Addition of [$NaNO_3$] to the reaction mixture increased the rate of reaction. The rate increased with decreasing percentage of acetic acid in the reaction medium. The product of oxidation was identified as benzil. The Arrhenius and activation parameters were calculated. The probable mechanism for oxidation of benzoin by NBS was proposed and a rate-law explaining all observed experimental facts was deduced.

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