

2-Acetamidophenol oxidation kinetics by N-bromo succinamide in perchloric acid medium

Jayadevappa H.P^{*1}.

^{*1}Department of Chemistry, Yuvaraja's College, University of Mysore, Mysuru 570 006, Karnataka, INDIA

Date of Submission: 30-07-2020

Date of Acceptance: 09-08-2020

ABSTRACT: 2-Acetamidophenol oxidation kinetics by N-bromo succinamide in perchloric acid medium has been studied at 303K. The oxidation products were tested and reaction stoichiometry was determined. The observed rate of reaction was a first order dependence on oxidant, fractional order on substrate and inverse fractional order on $[H^+]$. A slight negative effect of dielectric constant has been observed. With ionic strength the unchanged rate indicate involvement of non ionic species in rate determining step. The kinetic studies were performed at different temperature and thermodynamic parameters were computed. A mechanism consistent of reaction with observed parameters is proposed. Rate law is derived.

KEYWORDS: 2-Acetamidophenol, N-bromo succinamide, stoichiometry, dielectric constant, rate law.

I. INTRODUCTION

N-bromo succinamide (NBS), a potent oxidant belongs to the group of N-Halo amides which are used in the quantitative determination of a variety of organic compounds¹⁻³. As halogen in the +1 state, the N-haloimides are used for bromination and oxidation of many substrates⁴. Mild oxidising property of NBS has been exploited for oxidation reactions in both acidic and alkaline medium⁵⁻⁷.

2-Acetamidophenol (AP) or N-(2-Hydroxy-phenyl)acetamide is an isomer of analgesic drug 4-hydroxyacetanilide (paracetamol). It belongs to the class of aminophenols. The oxidation kinetics of paracetamol using mild oxidants and catalytic effect on oxidation was extensively studied^{8,9}. Hence in the present study we were encouraged to know 2-Acetamidophenol oxidation mechanism by N-bromo succinamide in perchloric acid medium¹⁰.

II. MATERIAL AND METHODS

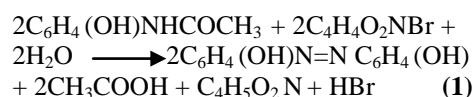
Experimental: A solution of the oxidant NBS (E. Merck sample purified¹¹) in water was standardized by the iodometric method and preserved in brown

bottle to prevent any further photochemical deterioration. Freshly prepared aqueous solution of the substrate AP (Sigma-Aldrich) of required strength was used each time. The other reagents used were of analytical grade. Conductivity water was used for the kinetic studies. Ionic strength was maintained using concentrated solution of sodium perchlorate. Methanol was added to maintain the dielectric constant. To keep pseudo first-order conditions excess of AP over NBS was maintained.

Kinetic measurements: A mixture of solutions of AP, and $NaClO_4$ in required amounts, along with requisite volume of water to keep the total volume constant for all runs is taken in a glass-stoppered Pyrex boiling tube and thermostated at 303K. Required amount of equilibrated solution of NBS was added to the mixture and shaken appropriately. The progress of reaction was studied iodometrically by the estimation of unreacted NBS in a measured aliquot (mL) of the reaction mixture with time, up to about two half-lives. The pseudo first-order rate constants calculated from the plots of $\log [NBS]$ against time are reproducible within $\pm 4\%$.

III. STOICHIOMETRY AND PRODUCT ANALYSIS

The kinetic runs performed by keeping excess of AP over NBS at 303 K. It confirm the following stoichiometry that two moles of AP consumed two moles of NBS.



The products of reaction were extracted with ether. One of the oxidation product of substrate 2,2¹-dihydroxy azobenzene was identified from the ether layer by Pausacker and Scroggie method¹². Another product acetic acid was confirmed by spot tests¹³. The reduction product of NBS, succinamide was extracted with ethyl acetate and confirmed by TLC.

IV. RESULTS AND DISCUSSION

The kinetic runs were performed under pseudo first order conditions by keeping an excess of substrate over NBS. The reaction between AP and NBS was investigated at several initial concentrations of the reactants at constant temperature (303K)

Effect of reactants on the rate of reaction: At fixed [AP], and temperature, plot of $\log[\text{NBS}]$ versus time was linear (Table -1) indicating the first order rate in [NBS]. The values of pseudo first order rate constant k' were constant for varying [NBS] (Table -1). The k' values increased with increase in $[\text{AP}]_0$ (Table -1). The plot of $\log k'$ versus $\log [\text{AP}]_0$ was linear (Figure -1) with a slope

of 0.255 indicate fractional-order dependence on $[\text{AP}]_0$.

Effect of pH on the rate of reaction: With an increase in pH of reaction mixture by adding HCl, the rate decrease with increase in pH showing inverse fractional order dependence on $[\text{H}^+]$ (Table -1) (Figure -1).

Effect of ionic strength on the rate of reaction: The ionic strength of the reaction mixture varied using a saturated solution of $\text{NaClO}_4 (1.0 \times 10^{-3} \text{ to } 10.0 \times 10^{-3} \text{ mol dm}^{-3})$. This indicates that ionic strength had no effect on the rate.

Table-1 Effect of oxidant, substrate and acid concentration on rate

$10^4 [\text{NBS}]$ mol dm ⁻³	$10^3 [\text{AP}]$ mol dm ⁻³	$10^3 [\text{HClO}_4]$ mol dm ⁻³	$k' \cdot 10^4 \text{S}^{-1}$
3	6	0	7.5432
6	6	0	7.5254
9	6	0	7.5252
12	6	0	7.5312
6	3	0	5.5245
6	6	0	7.5254
6	9	0	9.8362
6	12	0	12.456
6	6	3	9.2205
6	6	6	7.5254
6	6	9	5.8523
6	6	12	4.7252

$[\text{NBS}] = 6 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{AP}] = 6 \times 10^{-3} \text{ mol dm}^{-3}$,
 $[\text{H}^+] = 6 \times 10^{-3} \text{ mol dm}^{-3}$, $\mu = 0.5 \text{ mol/dm}^{-3}$.

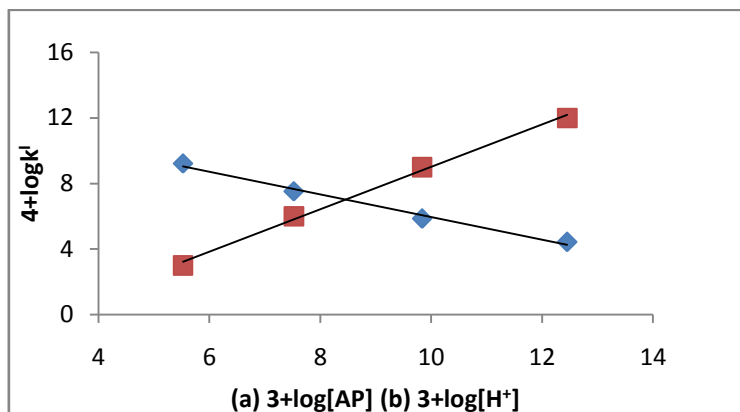


Figure-1 Effect of substrate and acid concentration on rate

Test for free radicals: The absence of in situ formation of free radicals species in the reaction sequence was confirmed by the addition of the reaction mixtures to aqueous acrylamide solution which did not initiate polymerization.

Effect of temperature on the rate of reaction: The kinetic runs were performed by

varying temperature from 298 K to 313 K and the values of k' were determined (Table -2) from pseudo-first-order plots. From the Arrhenius plot of $\log k'$ versus $1/T$ (Fig-2) the energy of activation (E_a) was calculated. From the value of E_a , the other thermodynamic parameters, ΔH^\ddagger , ΔG^\ddagger , and ΔS^\ddagger were calculated (Table-2).

Table-2 Effect of temperature and activation parameters on rate

Temperature (K)	$K^{-1} \cdot 10^4 (S^{-1})$	Thermodynamic parameter
298	6.2205	$E_a = 21.2460 \text{ kJ mol}^{-1}$
303	7.5254	$\Delta H^\ddagger = 15.033 \text{ kJ mol}^{-1}$
308	8.8582	$\Delta S^\ddagger = -225.237 \text{ J K}^{-1} \text{ mol}^{-1}$
313	10.3456	$\Delta G^\ddagger = 85.5277 \text{ kJ mol}^{-1}$
318	12.2275	-

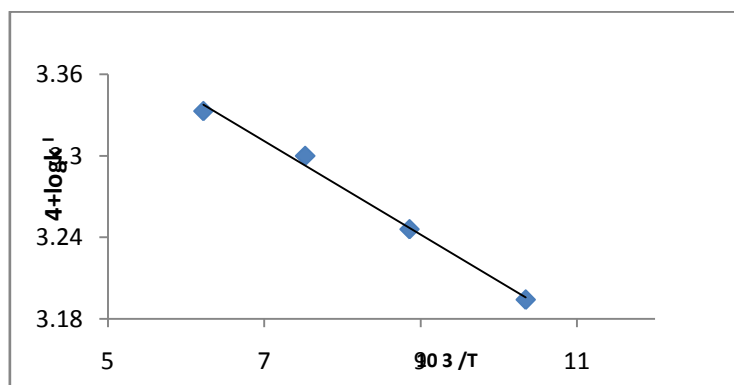


Figure-2 Effect of temperature on rate

Effect of dielectric constant on the rate of reaction: Kinetic measurements were performed by varying dielectric constant of the medium by adding methanol in different proportions (5 - 30 %, v/v). Increase in dielectric permittivity (D) of the

medium increased the rate of reaction (Table-3). The plot of $\log k'$ versus $1/D$ is linear with a negative slope. Methanol was ionized to very slight extent under the experimental conditions (<1%) as confirmed by the blank experiments

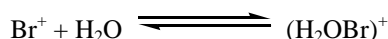
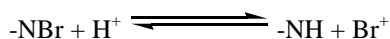
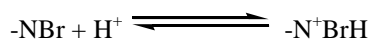
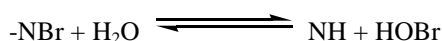
Table-2 Effect of dielectric constant on rate

MeOH % v/v	D	10 ² /D	K ¹ 10 ⁴ S ⁻¹
0	76.7	1.30	7.52
10	72.4	1.39	7.22
20	67.4	1.47	6.85
30	62.7	1.60	6.54
40	58.1	1.72	6.31

[NBS] = 6 x 10⁻⁴ mol dm⁻³, [AP] = 6 x 10⁻³ mol dm⁻³,
 [H⁺] = 6 x 10⁻³ mol dm⁻³, μ = 0.5 mol/dm³.

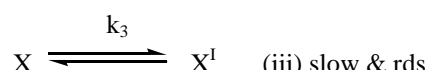
V. RATE LAW FOR THE OXIDATION OF AP BY NBS

NBS behaves as a source of positive halogen in aqueous solution and this reagent has been exploited as an oxidant for a variety of substrates in both acid and alkali solutions. It gets reduced to succinamide thereby acts as mild oxidant with a two electron change¹⁴⁻²¹. It produces different ionic species with following equilibria in aqueous acidic solution.



The negative effect of [H⁺] on the reaction rate observed in the present studies allows us to assume effect of [H⁺] on the reaction rate. It allows us to assume either protonated NBS, Br⁺ or (H₂OBr)⁺, or HOBr as active oxidizing species, and negative effect of the initially added product, succinimide restricts us to take Br⁺ as the oxidizing species. On the basis of observed kinetic data and above discussions, a probable mechanism (Scheme -1) is proposed for the oxidation. In scheme -2 the detailed plausible mechanism of reaction is picturized.

Let NBS represent the active oxidant, AP represent the substrate and X and X^I represent the intermediate complex species. The oxidation reaction is initiated by NBS through the attack of substrate to give an intermediate complex X. This complex eliminates a proton in the rate determining step to give the complex X^I which further reacts to give products.



differential rate equation is

$$\frac{d[\text{NBS}]}{dt} = k_3 [\text{X}] \quad (6)$$

Let [NBS]_t be the effective total concentration of NBS, then

$$[\text{NBS}]_t = [\text{HOBr}] + [\text{H}_2\text{OBr}^+] + [\text{X}] \quad (7)$$

$$[\text{NBS}]_t = ([\text{HOBr}][\text{H}^+])/k_1 + \frac{[\text{X}]}{k_2[\text{AP}]} + [\text{X}] \quad (8)$$

On solving for X,

$$[\text{X}] = \frac{k_1 k_2 [\text{NBS}] [\text{AP}]}{[\text{H}^+] k_1 (1 + k_2 [\text{AP}])} \quad (9)$$

$$\frac{d[\text{CAT}]}{dt} = \frac{k_1 k_2 k_3 [\text{NBS}]_t [\text{AP}]}{[\text{H}^+] + k_1 (1 + k_2 [\text{AP}])} \quad (10)$$

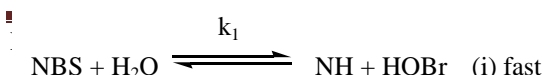
The rate law derived agrees with the experimental results that a first, fractional and inverse fractional order dependence of reaction rate on [NBS]₀, [AP]₀ and [H⁺] respectively.

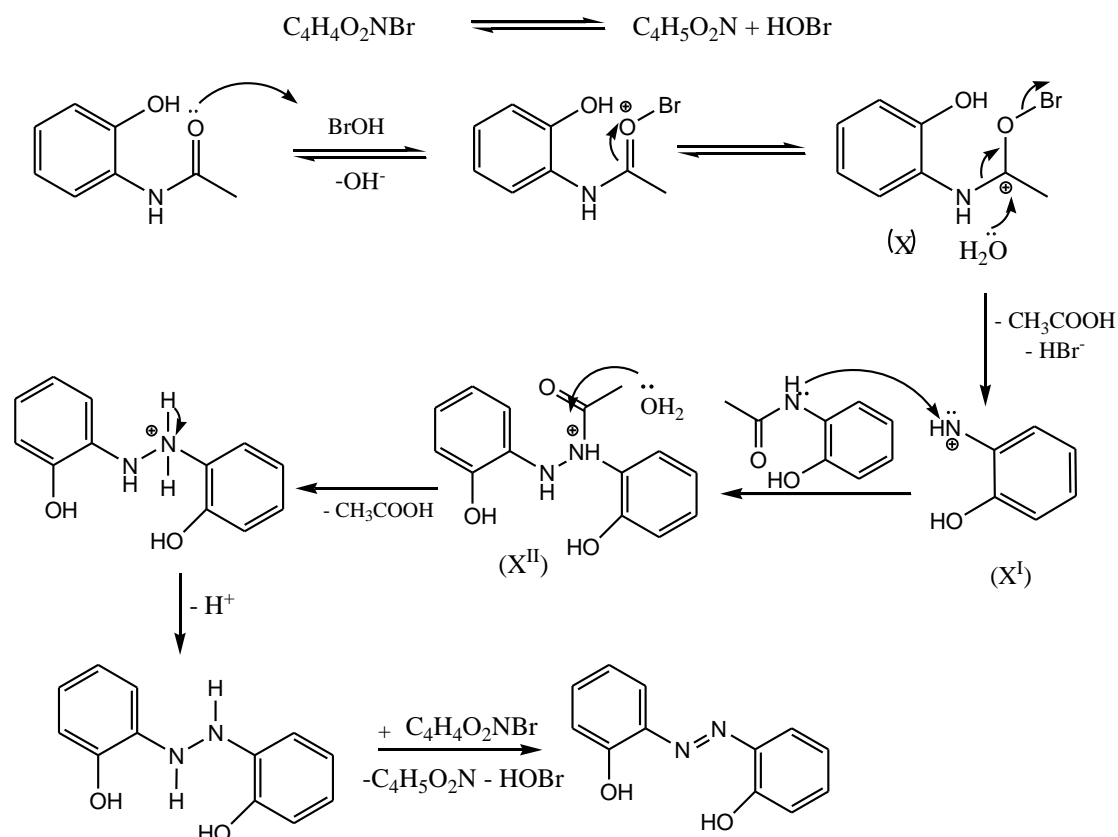
Since rate = k^I [NBS]₀, from equation (9) we have,

$$k^{\text{I}} = \frac{k_1 k_2 k_3 [\text{AP}]}{[\text{H}^+] + k_1 (1 + k_2 [\text{AP}])} \quad (11)$$

$$\frac{1}{k^{\text{I}}} = \frac{1}{k_2 k_3 [\text{AP}]} \left\{ \frac{[\text{H}^+]}{k_1} + 1 \right\} + \frac{1}{k_3} \quad (12)$$

From equations (11) and (12), plots of 1/k^I versus 1/[AP] and 1/k^I versus [H⁺] were linear (Figure 2). The values of k₁, k₂ and k₃ were calculated from the slopes and intercepts.





The dielectric constant of the medium was varied by adding methanol in different proportions (0 - 40 %, v/v). The dielectric effect is negligible²²⁻²⁵. The reduction product succinamide when added fails to change the rate. This indicates its non involvement in pre-equilibrium. The rate remains same on varying ionic strength of the medium indicating the involvement of non-ionic species in the rate determining step. Bromide ions have no significant effect on the rate of reaction. Further the proposed mechanism is supported by the thermodynamic parameters computed from the experimental results. Formation of a properly ordered compact transition state complex with lesser degrees of freedom is supported by large negative value of entropy of activation and moderate positive values of free energy of activation and enthalpy of activation.

VI. CONCLUSION

The redox reaction between NBS-AP has been carried out in aqueous medium. The reaction stoichiometry of 1:1 (eq.1) involving the AP oxidation by NBS has been observed. 2,2'-dihydroxy azobenzene and acetic acid are the products of oxidation. The effect of dielectric constant and halide ions on reaction rate was

studied. From the Arrhenius plots the thermodynamic parameters, E_a , ΔH^\ddagger , ΔG^\ddagger , and ΔS^\ddagger have been computed. For the observed parameters a consistent mechanism has been proposed and rate law was derived

ACKNOWLEDGEMENT : The author gratitude to the Yuvaraja's College, University of Mysore, Mysore for providing laboratory facilities to perform the kinetic study.

REFERENCES

- [1]. Seliwanow, T., Ber. Deut. Chem. Ges., **26**, 423 (1983)
- [2]. Wohl, A. and Jaschinowski, K., Ber. Deut. Chem. Ges., **74**, 1243 (1941)
- [3]. Ziegler, K., Spath, A., Schaaf, E., Schumann, W. and Winkelmann, E., Justus Liebigs Ann. Chem., **551**, 80 (1942)
- [4]. Djerassi, C., Chem. Rev., **43**, 271 (1948)
- [5]. Arapahoe Chem. Inc. Technical Bulletin on "Positive Bromine Compounds", Boulder, Colorado, 1962.
- [6]. Horner, L. and Winkelmann, E.H., "Newer methods of preparative organic Chemistry", vol. 3,

- Academic Press, New York and London, 1964,
p.151;Angew.Chem., **71**,349(1959)
- [7]. Filler, R., Chem.Revs., **63**,21(1963)
- [8]. Ajay kumar Singh, Reena Negi, Bhawana Jain, Yokraj Katre, Surya Prakash Singh and Virender K.Sharma, Ind. Eng. Chem.Res.2009,132(1),285
- [9]. Ajay kumar Singh, Reena Negi, Yokraj Katre and Surya Prakash Singh j.Mol.Catal A,2009,302,36-42
- [10]. H. P. Jayadevappa, G. Nagendrappa. International Journal of Analytical, pharmaceutical and biomedical sciences., **2013**, 2(2), 49-55.
- [11]. C. H. Depuy, M. Isaks, K. L. Eilers, and G. F. Morris. J. Org. Chem. 29, 3503 (1964)
- [12]. K. H. Pausacker, J. G. Scroggie. J. Chem. Soc. **1954**, 4003.
- [13]. F. Feig. Spot tests in organic analysis, 5th ed. Elsevier, Amsterdam, **1956**, 376
- [14]. Ford. M.C. and Waters. W.A., J.Chem. Soc., 2240(1952)
- [15]. Adam. J. Gosselain. P.A. and Goldfinger. P., Nature, **171**, 704(1953)
- [16]. Skell. P.S. Tuleen D.L. and Readio. P.D., J.Am. Chem. Soc., **85**, 2850 (1963)
- [17]. Koenig. T. and Brewer. W., J. Am. Chem. Soc., **86**, 2728 (1964)
- [18]. Mcgrath. B.P. and Tedder. J.M., Proc. Chem. Soc. 80 (1961)
- [19]. F.D. Chattaway,J. Chem.soc., Perkin Trans I, **1**, 145, **1905**
- [20]. B. Wiberg, physical chemistry, wiley, New York, **1964**
- [21]. J. Casado, M. Aturo Lopwz-Quintela and F.M. Lorenzobarral, J. Chem. Educ., 63, 450, 1986
- [22]. E. S. Amis. Solvent Effects On Reaction Rates and Mechanism, Academic Press, New York., **1966**, 1672.
- [23]. Laidler. Chemical Kinetics, Tata Mc Graw-Hill, New Delhi, **1995**, 211.
- [24]. G. M. G. Ramananda, S. Ananda. Kinetics and mechanism of oxidation of o-toluidine by sodium -N-chloro benzene sulphonamide in acid medium. Asian. J. Chem, **1999**, 11(4), 1348-1352.
- [25]. G. Akerlof. J. Am. Chem. Soc, **1932**, 54, 4125.



**International Journal of Advances in
Engineering and Management**

ISSN: 2395-5252



IJAEM

Volume: 02

Issue: 01

DOI: 10.35629/5252

www.ijaem.net

Email id: ijaem.paper@gmail.com