Kinetics and mechanism of oxidation of p-nitrobenzaldehyde by potassium bromate in perchloric acid medium

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ABSTRACT

Oxidation of aromatic aldehydes has been studied by several workers. Aromatic aldehydes found to have wide applications in synthetic and pharmaceutical industries. Benzaldehydes are used as flavoring agents, in perfumes, in the manufacture of triphenylmethane dyes such as malachite green etc. and in the synthetic chemistry in the synthesis of other aromatic aldehydes and α,β unsaturated acids. Richard have studied and bacterial activity and found that these compounds are being used to preservatives in ophthalmic solutions. Due to their synthetic importance several workers have made attempts to study these compounds by different oxidants. Ketrolac, an analgesic and anti-inflammatory agent is equal to morphine sulphate on a weight to weight basis for the alleviation of post operative pain. Atorvastatin and Rosuvastatin calcium lowers the cholesterol levels. Both are synthesized from aromatic aldehyde (p-Fluorobenzaldehyde). In the light of above back ground, we will try to study kinetics and mechanism of proposed reactions of oxidation of benzaldehyde and substituted benzaldehydes by potassium bromate in acidic medium.

Keywords: Permanganate, kinetics, correlation analysis, mechanism, oxidation

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INTRODUCTION

 Several workers have reported the catalyzed and uncatalyzed oxidation of variety of substrates by potassium bromate in acidic medium and studied their mechanisms. Chemistry of bromate ion in aqueous acidic medium is of considerable interest due to its importance in mechanistic chemistry[1]. A review of potassium bromate oxidation of organic and inorganic compounds has been given here:

Oxidation of primary, secondary and tertiary alcohols by potassium bromate in acidic medium has been studied by several workers [2,3,4,5]. In the case of primary alcohols, the rate determining step was found to be decomposition of bromate ester and – CH bond cleavage was also observed. On the other hand during the oxidation of secondary alcohols by bromate, the formation of alcohol – bromate, ester with no C-H bond cleavage was observed. Oxidation of tertiary alcohols was studied by Reddi and Sundaram [6,7]. They suggested pre-equilibrium complexation between bromate and the substrate, yielding complexes which differ only by a proton, followed by rate determining carbonyl compound formation and an intermediate which is subsequently oxidized to give the products.

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Several workers have reported the kinetics and mechanism of catalyzed and uncatalyzed oxidation by potassium bromate of various compounds. Some other important organic and inorganic compounds studied so for are amines [8, 9], hydroxyl amine [10], hydrofluoric acid [11], Mn(II)- catalyzed oxidation of citric acid [12], Determination of Atenolol and its preparations by Acid-Base Titration in Non-aqueous Medium [13]. etc. However, a very few references are available to the best of our knowledge, on the kinetics and mechanism of the oxidation of p-nitrobenzaldehyde by potassium bromate in perchloric acid medium.

These studies are in a limited range and the data available in these studies are inadequate for a comparative study of oxidation of aromatic aldehydes by bromate ion in acidic medium. Secondly contradictory reaction mechanisms have been proposed by different workers. Hence the title reaction is proposed to investigate in order to arrive a plausible mechanism and to understand the redox chemistry of potassium bromate in perchloric acid medium.

MATERIALS AND METHODS

All the materials and methods used were same as described in chapter 2. For oxidizing p-nitrobenzaldehyde, potassium bromate stock solution (5.0×10^{-2} mol dm^{-3}) was prepared by dissolving exactly weighed quantity of potassium bromate in doubly distilled water. The solution was prepared fresh just before the use and standardized iodometrically. For use in kinetic runs a 0.2 or 0.5 mol dm^{-3} stock solution of p-nitrobenzaldehyde in doubly distilled water was prepared alternate days prior to use because on standing the aqueous solution of p-nitrobenzaldehyde was found to turn yellowish, deteriorate in strength and give irreproducible results. However, with a freshly prepared solution of p-nitrobenzaldehyde, no such complication was observed. Mercury (II) acetate stock solution (0.2 mol dm^{-3}) was prepared by dissolving exactly weighed quantity of mercury (II) acetate in doubly distilled water.

PRODUCT ANALYSIS

For obtaining and identifying the reaction product(s) the following procedure was used. In some experiments, relatively larger concentration of p-Nitrobenzaldehyde and potassium bromate with other experimental conditions being the same as in kinetic studies, were left standing at 313 – 323 K for over three days to ensure the completion of the reaction. After this period the organic product was extracted with ether several times, dried over anhydrous magnesium sulphate and the ether was evaporated. The main product was identified to be p-nitrobenzoic acid. The identity of the product was confirmed by (mp 239-242^{0}C) and (mmp 240-243^{0}C) and by comparison of IR spectra of isolated product and its authentic sample.

STOICHIOMETRY

No suitable method is available for the estimation of p-nitrobenzaldehyde, hence in all kinetic results reported in this chapter, p-nitrobenzaldehyde was in excess over potassium bromate and the stoichiometry was also determined under the experimental conditions where p-nitrobenzaldehyde (substrate) was in excess over the potassium bromate (oxidant). The suitable reaction mixtures were prepared and left at 313 K for over 24 hours to ensure complete oxidation of p-nitrobenzaldehyde. The unreacted potassium bromate was determined iodometrically and these results are given in Table 1. These results indicate that one mole of potassium bromate is consumed for three moles of p-nitrobenzaldehyde in agreement with the equation (1)

$$3NO_2C_6H_4CHO + BrO_3^- \longrightarrow 3\ NO_2C_6H_4COOH + Br^- \qquad \cdots\cdots\cdots(1)$$
p-nitrobenzaldehyde　　　　　　　　　p-nitrobenzoic acid
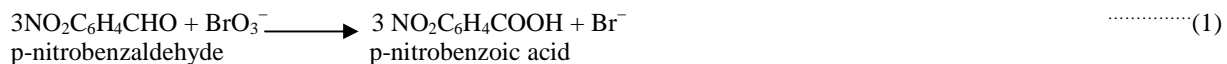
[KBrO$_3$]$_i$ represents the amount of KBrO$_3$ taken initially while Δ [KBrO$_3$] and Δ [PNB], i. e., Δ [p-nitrobenzaldehyde] represent the consumed amounts.

RESULTS

Entire kinetic study was carried out under pseudo first order conditions i.e., in all the kinetic runs the concentration of p-nitrobenzaldehyde was always at least ten times the concentration of potassium bromate and the reaction under such experimental conditions was characterised by the pseudo first order kinetics being first order with potassium bromate. The pseudo first order rate constant (k$_{obs}$) was evaluated for each experiment from the plot of log [KBrO$_3$] and time by following usual procedure. The pseudo first order plot in almost all cases was linear up to 70%

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completion of the reaction. The values of pseudo first order rate constant were reproducible within ± 5%. Initial rate constant was calculated from the plots of unconsumed [KBrO₃] versus time by plane mirror method.

POTASSIUM BROMATE DEPENDENCE

To study the dependence of the reaction rate on the concentration of potassium bromate, its concentration was varied in the range 1.0 to 5.0×10^{-3} mol dm^{-3} at fixed [p-nitrobenzaldehyde] = 5.0×10^{-2} mol dm^{-3}, [HClO₄] = 10.0×10^{-2} mol dm^{-3}, [NaClO₄] = 40.0×10^{-2} mol dm^{-3}, ionic strength = 50.0×10^{-2} mol dm^{-3} in 40% (v/v) aqueous acetic acid at 313 □ 0.1K in the presence of [mercuric acetate]=1.0×10^{-2} mol dm^{-3} which complexes bromide ions (one of the product of the reaction) preventing the in situ formation of molecular bromine. The results of kinetic runs, initial rates and pseudo first order rate constants at different initial concentrations of potassium bromate are given in Table 2. The order in potassium bromate was established by initial rate method. The plot of initial rate versus [potassium bromate] was a straight line passing through the origin showing thus the order in potassium bromate. Subsequently pseudo first order plots were made since the concentration of p-nitrobenzaldehyde was more than ten times the concentration of potassium bromate in each case. In each case good straight line was obtained and the values of pseudo first order rate constant (k$_{obs}$) were independent of the concentration of potassium bromated. The empirical rate law at constant [H$^+$] and excess p-nitrobenzaldehyde concentration is

$$\frac{-d[BrO_3^-]}{dt} = k_{obs}[BrO_3^-] \qquad\qquad\qquad …………… (2)$$

p-NITROBENZALDEHYDE DEPENDENCE

The dependence of the reaction rate on the concentration of p-nitrobenzaldehyde was studied by varying its concentration in the range 1.0 to 20.0×10^{-2} mol dm^{-3} at fixed [KBrO₃]=1.0×10^{-3} mol dm^{-3}, [HClO₄] = 10.0×10^{-2} mol dm^{-3}, [NaClO₄]= 40.0×10^{-2} mol dm^{-3}, ionic strength = 50.0×10^{-2} mol dm^{-3} in 40% (v/v) aqueous acetic acid at 313 □ 0.1K in the presence of [Hg (OAc)₂] =1.0×10^{-2} mol dm^{-3}. The results of kinetic runs and the values of pseudo first order rate constant (k$_{obs}$) are given in Table 3. The pseudo first order plots were made since the concentration of p-nitrobenzaldehyde was in excess, i.e., more than ten times the concentration of potassium bromate. In each case good straight line was obtained. The plot of pseudo first order rate constant (k$_{obs}$) versus [p-nitrobenzaldehyde] is a straight line passing through the origin. It shows that the order of the reaction with respect to p-nitrobenzaldehyde is also one. The empirical rate law is, therefore,

$$\frac{-d[BrO_3^-]}{dt} = k_2[BrO_3^-][p-nitrobenzaldehyde] \qquad\qquad …………… (3)$$

where k₂ is second order rate constant and k$_{obs}$ = k₂ [p-nitrobenzaldehyde]. The values of pseudo first order rate constant (k$_{obs}$) and second order rate constant (k₂) under different experimental conditions.

The unit orders with respect to [KBrO₃] and [p-nitrobenzaldehyde] indicate that probably they are not involved in the formation of any kind of complex or even if, the complex is formed, it was assumed to be highly unstable. Subsequently Michaelis – Menten type of reciprocal plot of 1/k$_{obs}$ versus 1/ [p-nitrobenzaldehyde] (k$_{obs}$ = pseudo first order rate constant) was linear passing through the origin. This indicates the absence of complex formation or lack of kinetically detectable complex between potassium bromate and p-nitrobenzaldehyde in perchloric acid medium.

MERCURIC ACETATE DEPENDENCE

The dependence of the reaction rate on the concentration of mercuric acetate was studied by varying its concentration in the range 1.0 to 5.0×10^{-2} mol dm^{-3} at fixed [KBrO₃]=1.0×10^{-3} mol dm^{-3}, [p-nitrobenzaldehyde] = 10.0×10^{-2} mol dm^{-3}, [HClO₄] = 10.0×10^{-2} mol dm^{-3}, [NaClO₄] = 40.0×10^{-2} mol dm^{-3}, ionic strength= 50.0×10^{-2} mol dm^{-3} in 40% (v/v) aqueous acetic acid at 313□ 0.1K. The results of kinetic runs and the values of pseudo first order rate constant (k$_{obs}$). These results indicate that there is no significant effect of mercuric acetate concentration on the rate. Thus the oxidation of p-nitrobenzaldehyde by potassium bromate is independent of the initial concentration of mercuric acetate which shows that the only function of mercuric acetate is to fix the generated bromine.

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HYDROGEN ION DEPENDENCE

The dependence of the reaction rate on the concentration of hydrogen ion was studied by varying the concentration of perchloric acid in a narrow range of 5.0 to 20.0 $\times 10^{-2}$ mol dm^{-3} at a constant ionic strength of 50.0×10^{-2} mol dm^{-3} using perchloric acid and sodium perchlorate mixture at fixed [KBrO$_3$] = 1.0×10^{-3} mol dm^{-3}, [p-nitrobenzaldehyde]= 5.0×10^{-2} mol dm^{-3} in 40% (v/v) aqueous acetic acid at 313□ 0.1 K in the presence of [Hg (OAc)$_2$] = 1.0×10^{-2} mol dm^{-3}. The results of kinetic runs and the values of pseudo first order rate constant (k$_{obs}$) are given in Table 5.5. The pseudo first order plots were made since the concentration of p-nitrobenzaldehyde was in excess, i.e., more than ten times the concentration of potassium bromate. In each case good straight line was obtained. These results indicate that the rate depends nearly on the first power of [H$^+$] in the range of 5.0 to 15.0×10^{-2} mol dm^{-3}, but exhibit higher order dependence on [H$^+$] at higher [acid], at constant ionic strength. The acid variation at constant ionic strength is limited to only 20.0×10^{-2} mol dm^{-3}. Beyond 20.0×10^{-2} mol dm^{-3} of perchloric acid, the dissociation of potassium bromate is considerable in our experimental conditions, making further investigation on acid dependence difficult. Hence quantitative interpretation of acid dependence has not been attempted.

IONIC STRENGTH DEPENDENCE

The dependence of the reaction rate on ionic strength was examined by varying the concentration of sodium perchlorate in the range 0.0 to 40.0×10^{-2} mol dm^{-3} at fixed [KBrO$_3$]= 1.0×10^{-3} mol dm^{-3}, [p-nitrobenzaldehyde] = 5.0×10^{-2} mol dm^{-3}, [HClO$_4$] = 10.0×10^{-2} mol dm^{-3} in 40% (v/v) aqueous acetic acid at 313 □ 0.1K in the presence of [Hg(OAc)$_2$] = 1.0×10^{-2} mol dm^{-3}. The results of kinetic runs and the values of pseudo first order rate constant (k$_{obs}$) are given in Table 5.6 These results indicate that the rate of reaction decreased on increasing the ionic strength. The results of ionic strength variation suggest that the oxidation of p-nitrobenzaldehyde with potassium bromate is the reaction between ions of opposite charge, i.e., between cation and anion. Hence this rules out the possibility of dipole - dipole and ion - dipole interaction in the oxidation of p-nitrobenzaldehyde with potassium bromate.

DIELECTRIC CONSTANT DEPENDENCE

The dependence of the reaction rate on dielectric constant was studied by varying the composition of the solvent mixture. It is done by varying the percentage of acetic acid in AcOH:H$_2$O mixture in the range 10% to 50% (v/v) aqueous acetic acid at fixed [KBrO$_3$]= 1.0×10^{-3} mol dm^{-3}, [p-nitrobenzaldehyde]= 10.0×10^{-2} mol dm^{-3}, [HClO$_4$] = 10.0×10^{-2} mol dm^{-3}, [NaClO$_4$] = 40.0×10^{-2} mol dm^{-3}, ionic strength = 50.0×10^{-2} mol dm^{-3} at 313 □ 0.1K in the presence of [Hg(OAc)$_2$] = 1.0×10^{-2} mol dm^{-3}. The results of kinetic runs and the values of pseudo first order rate constant (k$_{obs}$) are given. The values of dielectric constant for various proportions of acetic acid as reported earlier are used. These results indicate that the values of pseudo first order rate constant increases as the percentage of acetic acid in AcOH: H$_2$O solvent mixture increases. Thus the reaction rate of the oxidation of p-nitrobenzaldehyde by potassium bromate increases as the dielectric constant of the solvent mixture decreases. The Amis plot of log k$_2$ versus 1/D was linear with a positive slope which is in agreement that the oxidation of p-nitrobenzaldehyde with potassium bromate is the reaction between ions of opposite charge, i.e., between cation and anion. Hence this also rules out the possibility of dipole - dipole and ion - dipole interaction in the oxidation of p-nitrobenzaldehyde with potassium bromate.

TEMPERATURE DEPENDENCE

To determine the temperature coefficient and thermodynamic activation parameters such as energy of activation (Ea), frequency factor (A), free energy of activation (ΔG), entropy of activation (ΔS) and enthalpy of activation (ΔH), the reaction was carried out at three different temperatures, i.e., 303, 313 and 323K. The results of the kinetic runs and the values of pseudo first order rate constant (k$_{obs}$) for temperature dependence are tabulated respectively. The values of pseudo first order rate constant (k$_{obs}$) and second order rate constant (k$_2$) at different temperatures are collected. These results indicate that the values of pseudo first order rate constant (k$_{obs}$) and second order rate constant (k$_2$) increase as the temperature increases. The values of temperature T, reciprocal of temperature (1/T), second order rate constant (k$_2$) and log k$_2$ are tabulated. The plot of log k$_2$ versus 1/T which is linear showing that the Arrhenius equation relating to temperature with specific rate is followed. The data obtained from the investigation of reaction rate at different temperatures were used to calculate the values of the temperature coefficient and thermodynamic activation parameters such as energy of activation (Ea), frequency factor (A), free energy of activation (ΔG), entropy of activation (ΔS) and enthalpy of activation (ΔH).

ABSENCE OF FREE RADICALS IN THE REACTION MIXTURE

The intervention of free radicals in the reaction was studied by keeping the reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, for one hour in an inert atmosphere of nitrogen. On

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diluting the reaction mixture with methanol, there was no formation of precipitate, indicating the absence of free radical intervention in the reaction. The blank experiments of either p-nitrobenzaldehyde or potassium bromate with acrylonitrile alone did not induce polymerization under the same condition.

The results obtained for the oxidation of p-nitrobenzaldehyde by potassium bromate in perchloric acid – acetic acid medium is summarized as follows.

1. The reaction proceeds with a measurable velocity at 313 K.
2. The oxidation of p-nitrobenzaldehyde by potassium bromate was found to follow first order kinetics with respect to potassium bromate (oxidant). The initial rate increases with the increase in [potassium bromate]. The plot of initial rate versus [$KBrO_3$] was a straight line passing through the origin, thus showing the order in potassium bromate is one. Subsequently the values of pseudo first order rate constant (k_{obs}) were independent of the concentration of potassium bromate thus showing the order in potassium bromate is one.
3. The oxidation of p-nitrobenzaldehyde by potassium bromate was found to follow first order kinetics with respect to p-nitrobenzaldehyde (substrate). The plot of pseudo first order rate constant (k_{obs}) versus [p-nitrobenzaldehyde] is a straight line passing through the origin. It indicates that the order of the reaction with respect to p-nitrobenzaldehyde is also one.

The unit orders with respect to [$KBrO_3$] and [p-nitrobenzaldehyde] indicate that probably they are not involved in the formation of any kind of complex, or even if the complex is formed, it was assumed to be highly unstable. The Michaelis – Menten type of reciprocal plot of $1/k_{obs}$ versus $1/$ [p-nitrobenzaldehyde] (k_{obs} = pseudo first order rate constant) was linear passing through the origin. This indicates the absence of complex formation or lack of kinetically detectable complex between potassium bromate and p-nitrobenzaldehyde in acidic medium.

4. There is no significant effect of mercuric acetate concentration on the rate of reaction. Thus the oxidation of p-nitrobenzaldehyde by potassium bromate is independent of the initial concentration of mercuric acetate which shows that the only function of mercuric acetate is to fix the generated bromine.
5. The results indicate that the rate depends nearly on the first power of [H^+] in the range of 5.0 to 15.0×10^{-2} mol dm^{-3} but exhibit higher order dependence on [H^+] at higher [acid] at constant ionic strength. The acid variation at constant ionic strength is limited to only 20.0×10^{-2} mol dm^{-3}. Beyond 20.0×10^{-2} mol dm^{-3} perchloric acid, the dissociation of potassium bromate is considerable making further investigation of acid dependence difficult. Hence quantitative interpretation of acid dependence has not been attempted.
6. The results indicate that the rate of reaction decreased on increasing the ionic strength. The results of ionic strength variation suggest that the oxidation of p-nitrobenzaldehyde with potassium bromate is the reaction between ions of opposite charge, i.e., between cation and anion, Hence it rules out the possibility of dipole –dipole and ion-dipole interaction in the oxidation of p-nitrobenzaldehyde with potassium bromate in perchloric acid medium.
7. The values of pseudo first order rate constant increases as the percentage of acetic acid in AcOH: H_2O (solvent mixture) increases. The Amis plot of log k_2 versus $1/D$ was linear with a positive slope, which is in agreement that the oxidation of p-nitrobenzaldehyde with potassium bromate is the reaction between ions of opposite charge, i.e., between cation and anion. Hence it also rules out the possibility of dipole - dipole and ion - dipole interaction in the oxidation of p-nitrobenzaldehyde with potassium bromate in perchloric acid medium.
8. The values of the temperature coefficient and thermodynamic activation parameters such as energy of activation (Ea), frequency factor (A), free energy of activation (ΔG), entropy of activation (ΔS) and enthalpy of activation (ΔH) of the reaction are given below.

Temperature coefficient	(Ea)kJ mol^{-1}	(log A) mol^{-1} dm^3 sec^{-1}	(ΔG) kJ mol^{-1}	(ΔS) JK^{-1} mol^{-1}	(ΔH) kJ mol^{-1}
2.42	71.68	9.9990	88.50	- 62.22	69.03

9. The results indicate that one mole of potassium bromate is consumed for three moles of p-nitrobenzaldehyde in agreement with the following equation.
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$$3NO_2C_6H_4CHO + BrO_3^- \rightarrow 3\ NO_2C_6H_4COOH + Br^-$$
p-nitrobenzaldehyde   p-nitrobenzoic acid
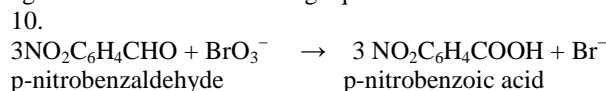
11. The main product of oxidation of p-nitrobenzaldehyde with potassium bromate in perchloric acid medium is p-nitrobenzoic acid.
12. Addition of monomers like acrylonitrile to the reaction mixture under inert condition did not induce any polymerization. This indicates the absence of free radicals in the reaction mixture. Therefore, there is no possibility

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of free radical mechanism in the oxidation of p-nitrobenzaldehyde with potassium bromate in acetic acid – perchloric acid medium.

TABLE 1 STOICHIOMETRY OF POTASSIUM BROMATE p-NITROBENZALDEHYDE (PNB) REACTION
$[HClO_4]$ = 0.1M, $[Hg(OAc)_2]$ = 0.01M, AcOH: H_2O = 40:60 Temperature 313K

S. N.	10^3 [PNB] mol dm^{-3}	$10^3[KBrO_3]_i$ mol dm^{-3}	$10^3 \Delta$ [KBrO$_3$] mol dm^{-3}	Δ [PNB] Δ [KBrO$_3$]
1	1.0	1.0	0.36	2.78
2	1.5	1.0	0.52	2.88
3	2.0	1.0	0.74	2.70
4	2.5	1.0	0.86	2.90
5	3.0	2.0	1.06	2.83
6	3.5	2.0	1.18	2.97
7	4.0	2.0	1.38	2.90
8	4.5	2.0	1.54	2.92

TABLE 2 VARIATION OF POTASSIUM BROMATE CONCENTRATION

[p-Nitro benzaldehyde] = $5.0 \times 10^{-2}M$ $[HClO_4] = 10.0 \times 10^{-2}M$ $[NaClO_4] = 40.0 \times 10^{-2}M$
I = $50.0 \times 10^{-2}M$ $[Hg(OAc)_2] = 1.0 \times 10^{-2}M$ AcOH : H_2O = 40:60
Aliquots = 5 ml   Temperature 313 K

10^3[Hypo],M	3.0			6.0			12.0		
10^3[KBrO$_3$],M	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Time in minutes	Volume of Hypo in ml.								
0	10.00	15.00	20.00	12.50	15.00	17.50	10.00	11.25	12.50
2	9.30	14.10	18.50	11.25	14.10	15.80	9.25	10.50	11.10
5	8.50	13.00	17.10	10.60	13.00	14.30	8.45	9.30	10.50
10	7.30	11.00	14.50	8.90	10.80	12.30	7.25	8.20	8.70
15	6.20	9.30	12.30	7.80	9.10	10.50	6.10	7.00	7.60
20	5.20	8.00	10.30	6.60	7.80	9.00	5.10	5.90	6.40
25	4.50	6.80	8.90	5.75	6.60	7.60	4.40	5.00	5.60
30	3.80	5.80	7.50	4.80	5.60	6.70	3.70	4.30	4.60
10^7(-dc/dt),Ms^{-1}	5.30	8.00	10.60	13.15	15.80	18.30	21.10	23.55	26.20
10^4 k$_{obs}$, s^{-1}	5.36	5.20	5.40	5.30	5.40	5.30	5.50	5.35	5.50

TABLE 3 VARIATION OF p-NITROBENZALDEHYDE (PNB) CONCENTRATION

$[KBrO_3] = 1.0 \times 10^{-3}M$ $[HClO_4] = 10.0 \times 10^{-2}M$ $[NaClO_4] = 40.0 \times 10^{-2}M$
I = $50.0 \times 10^{-2}M$ $[Hg(OAc)_2] = 1.0 \times 10^{-2}M$ AcOH : H_2O = 40:60
Aliquots = 5 ml   Temperature 313 K

10^2[PNB],M	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Time in minutes	Volume in ml. of 3.0×10^{-3} M Hypo									
0	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00	10.00
2	9.90	9.70	9.60	9.50	9.30	9.25	9.20	9.10	9.00	8.80
5	9.60	9.35	9.00	8.80	8.60	8.30	8.10	7.80	7.60	7.30
10	9.30	8.70	8.20	7.70	7.40	6.80	6.50	6.15	5.70	5.20
15	8.80	8.20	7.40	6.70	6.30	5.70	5.30	4.70	4.40	3.90
20	8.60	7.70	6.80	6.10	5.30	4.60	4.30	3.70	3.20	2.80
25	8.40	7.20	6.20	5.30	4.60	3.90	3.40	2.80	2.50	2.10
30	8.20	6.70	5.60	4.70	3.80	3.10	2.60	2.20	2.20	1.50
10^4 k$_{obs}$, s^{-1}	1.10	2.10	3.22	4.20	5.38	6.50	7.48	8.42	9.50	10.60

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