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Kinetics and Mechanism of the Oxidation of Neomenthol by Potassium Bromate in Acidic Solution

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Abstract

Present study was focused on the analysis of kinetics and mechanism of oxidation of neomenthol by potassium bromate in acidic medium. For oxidizing neomenthol, 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 suitable reaction mixtures were prepared and left at 313 K for over 24 hours to ensure complete oxidation of neomenthol. The unreacted potassium bromate was determined iodometrically and the results indicate that one mole of potassium bromate is consumed for every three moles of neomenthol which leads to the formation of menthone (ketone).

Keywords: Oxidation, Reaction Kinetics and Mechanism, Stoichiometry

1. Introduction

The oxidation of cyclic alcohols have been studied by various oxidizing agents so far such as N-bromoacetamide, N-bromosaccharin, t-butyl hypochlorite, bis-(2,2-bipyridyl) copper(II) permanganate, cerium(IV) catalyzed by chromium(III), chromium(VI) in presence of oxalic acid, aqueous chlorine, dioxo ruthenium(VI) complex, potassium hexacyanoferrate(III), pyridinium fluoro chromate, sodium bromate and ferric chloride etc.[1] On account of its anaesthetic and antiseptic action, pleasant odour and cooling taste, neoneomenthol finds wide applications in industrial and pharmaceutical fields.[3] Despite its industrial and pharmaceutical importance, only few kinetic investigations of the oxidation of neomenthol with aqueous chlorine only appear to have been studied[4]. According to literature cited, no significant work has been reported related to the oxidation kinetics of terpenes or terpenoids in general and neomenthol in particular with potassium bromate in acidic medium. For quite some times we have been interested in the study of oxidation kinetics of organic substrates by potassium bromate in acidic medium[7].

2. Materials and Methods

2.1 Reagents

2.1.1 Potassium bromate, $KBrO_3$: An aqueous solution of potassium bromate ($KBrO_3$) (Merck) was prepared by weighing and dissolving in doubly distilled water. The strength of prepared potassium bromate solution was checked iodometrically for active bromine by standardizing it against sodium thiosulphate (hypo) solution which was already standardized against copper sulphate, $CuSO_4.5H_2O$ (S.D. fine Chem. Ltd) solution. The prepared solution of potassium bromate was always stored in a measuring flask coated from outside by black japan to prevent its photochemical deterioration[10].

2.1.2 Terpenes or terpenoidsL Menthol, neomenthol, borneol and isoborneol were the terpenes or terpenoids which were used for the present study. These terpenes or terpenoids belong to the class of cyclic alcohols. All the terpenes or terpenoids were analytical reagent grade. Menthol and neomenthol were the make of Fluka Puriss. Borneol and isoborneol were the make of Lancaster and Willson respectively. These terpenes or terpenoids were purified by redistillation or recrystallisation from water and purity was checked by their boiling points before use. The solution of each terpenes or terpenoids was prepared by dissolving the appropriate quantity of its sample in doubly distilled water[9]. The solution was prepared in a measuring flask coated from outside by black japan and the measuring flask was placed in a dark atmosphere in the refrigerator. These solutions were used within two or three days to avoid any photochemical oxidation. At least for a week, these solutions did not show any decomposition. As a precautionary measure their stock solution were prepared on the alternate days and kept in the refrigerator to avoid any photochemical oxidation[26].

2.1.3 Perchloric acid, $HClO_4$: Perchloric acid used was of analytical reagent grade (70% Merck). No chloride impurity was detected with silver nitrate solution. The solution of perchloric acid was prepared directly dissolving appropriate volume of sample in doubly distilled water which was standardized with the help of standard solution of sodium hydroxide (S. D. Fine Chem. Ltd) using phenolphthalein as an indicator. Perchloric acid is used as a source of hydrogen ion in the present investigation[6].

2.1.4 Acetic acid, CH_3COOH: Glacial acetic acid (99.7%, BDH) was used for the preparation of buffer solution. It was diluted with doubly distilled water to prepare the acetic acid solution of requisite strength[3].

2.1.5 Mercuric acetate, $Hg(CH_3COO)_2$: Mercuric acetate (Merck) was dissolved firstly in glacial acetic acid (99.7% BDH) and then made up to its required volume with doubly distilled water but acetic acid strength in mercuric acetate solution should not be more than 10 percent[26].

2.1.5 Potassium iodide, KI: 4% solution of potassium iodide (Merck) was prepared fresh each day by dissolving appropriate weighed amount of potassium iodide in doubly distilled water[7].

2.1.6 Sodium thiosulphate, $Na_2S2O_3.5H_2O$ (HYPO): Appropriate weighed amount of sodium thiosulphate (Merck) was dissolved in doubly distilled water and standardized against standard copper sulphate, $CuSO_4.5H_2O$ (S. D. Fine Chem. Ltd) solution by iodometric titration using starch solution as an indicator. Sodium thiosulphate (hypo) solution was used to estimate the concentration of remaining potassium bromate iodometrically using starch solution as an indicator during the kinetic investigation.

2.1.7 Starch: 1% starch (s. d. fine Chem. Ltd) solution was prepared in doubly distilled water, a fresh each day and was used as an internal indicator in the present investigation[10].

2.1.8 Sulphuric acid, H_2SO_4: (2N) sulphuric acid was prepared by dissolving appropriate volume of its sample (laboratory reagent grade) in doubly distilled water[26].

2.1.9 Doubly distilled water (Conductivity water): Doubly distilled water was prepared by redistilling distilled water in corning glass round bottom flask containing few crystals of potassium permanganate and potassium hydroxides. Doubly distilled water was stored in flasks made of corning glass[26].

2.1.10 Acrylonitrile C_3H_3N (OR) ($CH_2 = CH - C\equiv N$): Acrylonitrile is also known as acrylic acid nitrile or venyl cyanide. Acrylonitrile used was of analytical reagent grade (Merck). It is liquid with boiling point 77 – 78°C. The solution of acrylonitrile was prepared directly by weighing and dissolving the weighed amount in doubly distilled water. It is easily soluble in water[10].

2.2 Method of Study: During the course of study, for all the reactions conical and measuring flasks coated from outside by black japan, were used to avoid any photochemical reaction. Doubly distilled water was used throughout the investigation to prevent any foreign ion effect. All the measuring flasks and reaction vessels were of corning glass, jena glass or borosil with well glass stoppers. The measuring flasks, reaction vessels, the burettes, pipettes etc. used were of standard quality. The glass wares used were pretreated with chromic acid and rinsed with doubly distilled water before their use. An electrically operated thermostatic water-bath was used. It was provided with sufficient thermal lagging, suitable heaters and stirrers with proper water circulation for continuous work. Contact thermometer (Jumo, D.P.B German) worked in conjugation with an electric relay maintained at the required temperatures accurately with a precision of ± 0.1°C. The temperatures were recorded by means of an accurate and sensitive thermometer, reading to tenths of a degree celcius. The actual progress of the reaction was monitored by estimating the amount of unconsumed potassium bromate ($KBrO_3$) in the reaction at regular time intervals, against standard solution of sodium thiosulphate (hypo) iodometrically. The reaction mixture containing requisite amount of all reactants, i.e., perchloric acid (which is used to maintain the hydrogen ion strength of the medium), sodium perchlorate (which is used to maintain the ionic strength of the medium), substrate, mercuric acetate, acrylonitrile (which is used to study the intervention of free radicals), doubly distilled water etc. except oxidant (potassium bromate) were kept in a conical flask coated from outside by black japan in the thermostatic water- bath at constant temperature with an accuracy of ± 0.1°C and fresh solution of oxidant (potassium bromate) was also kept in a separate conical flask within the same thermostatic water-bath at the same temperature. After thirty minutes when the reaction mixture has acquired the temperature of water-bath required amount of oxidant solution was sucked out by pipette and was poured in the conical flask which was already containing mixture of all other reactants (i.e.appropriate amounts of each perchloric acid, sodium perchlorate, substrate, mercuric acetate, acrylonitrile, doubly distilled water etc.) to initiate the reaction. The total volume of the reaction mixture was now (after addition of oxidant solution to the reaction mixture) 50 ml in each case The order of mixing of the reactants had no effect on the rate of reaction. As soon as half of the oxidant solution passed out from the pipette into reaction mixture, the watch was started to record time and immediately pipetted out aliquot amount (5ml) of reaction mixture and quickly transferred to a conical flask containing 5ml of 2% solution of potassium iodide, 10ml of 2N-sulphuric acid and a few drops of freshly prepared starch solution. The progress of the reaction was monitored by measuring unconsumed amount of potassium bromate iodometrically. The function of potassium iodide solution was to check the reaction .The remaining (i.e. unconsumed) amount of potassium bromate interacts with potassium iodide and liberates an equivalent amount of iodine from potassium iodide solution which was titrated against standard sodium thiosulphate solution, using starch as an indicator. The volume of sodium thiosulphate (hypo) solution corresponding to the iodine liberated by unreacted or unconsumed potassium bromate is noted. This provided reproducible results with marked accuracy. Added mercuric acetate did not interfere with

the reaction. It acts as a scavenger for any bromide ion formed in the reaction. It suppresses completely the oxidation by molecular bromine which would have been formed by the interaction of bromate with bromide formed in the reaction. Thus mercuric acetate ensures the oxidation purely through acid bromated reactions.

$KBrO_3 + 3H_2SO_4 + 6KI \rightarrow KBr + 3K_2SO_4 + 3H_2O + 3I_2$

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

2.3 Experimental: All the materials and methods used were same as described in chapter 2. For oxidizing neomenthol, 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[12]. For use in kinetic runs a 0.2 or 0.5 mol dm^{-3} stock solution of neomenthol in doubly distilled water was prepared alternate days prior to use because on standing the aqueous solutions of neomenthol were found to turn yellowish deteriorate in strength and give irreproducible results. However, with a freshly prepared solution of neomenthol, 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[85].

2.4 Stoichiometry: No suitable method is available for the estimation of neomenthol, hence in all kinetic results reported in this chapter, neomenthol was in excess over potassium bromate and the stoichiometry was also determined under the experimental conditions where neomenthol (substrate) was in excess over potassium bromate (oxidant). The suitable reaction mixtures were prepared and left at 313 K for over 24 hours to ensure complete oxidation of neomenthol[15]. The unreacted potassium bromate was determined iodometrically and the results are given in Table 1. The results indicate that one mole of potassium bromate is consumed for three moles of neomenthol in agreement with the equation (1) leading to the formation of menthone (ketone)

$$\underset{\text{Neomenthol}}{3C_9H_{18}CHOH} + BrO_3^- \rightarrow \underset{\text{Menthone}}{3C_9H_{18}CO} + Br^- + 3H_2O \qquad \text{……..(1)}$$

Table 1 Stoichiometry of Potassium bromate- Neomenthol reaction

10^3 [Neomenthol] mol dm^{-3}	$10^3[KBrO_3]_i$ mol dm^{-3}	10^3 $\Delta[KBrO_3]$ mol dm^{-3}	Δ [Neomenthol] / Δ [$KBrO_3$]
1.00	1.00	0.36	2.78
1.50	1.00	0.52	2.88
2.00	1.00	0.72	2.78
2.50	1.00	0.85	2.94
3.00	1.50	1.05	2.86
3.50	1.50	1.18	2.97
4.00	2.00	1.35	2.96
4.50	2.00	1.54	2.92

$[HCLO_4]$ = 0.1M, $[HG(OAC)_2]$ = 0.01M, ACOH: H_2O= 70:30 TEMPERATURE 313K

$[KBrO_3]$i represents the amount of $KBrO_3$ taken initially while Δ $[KBrO_3]$ and Δ [Neomenthol] represent the consumed amounts.

2.5 Product analysis: For obtaining and identifying the reaction product(s) the following procedure was used. In some experiments, relatively larger concentration of neomenthol 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[14]. 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 menthone by thin layer chromatography using benzene as solvent and by spraying with 2, 4-dinitrophenyl hydrazine. The identity of the product was confirmed by comparison of IR spectra of isolated product and its authentic sample.

3. Results

Entire kinetic study was carried out under pseudo first order conditions i.e., in all the kinetic runs the concentration of neomenthol was always at least ten times the concentration of potassium bromate and the reaction under such experimental conditions was characterized by the pseudo first order kinetics being first order with potassium bromate[4]. 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.[26] The pseudo first order plot in almost all cases was linear up to 70% completion of reaction. The values of pseudo first order rate constant were reproducible within ± 5%. Initial rate constant was calculated from the plots of unconsumed $[KBrO_3]$ versus time by plane mirror method.

3.1 Potassium bromate dependence: To study the dependence of the reaction rate of potassium bromate, its concentration was varied in the range 1.0 to 5.0 $\times10^{-3}$ mol dm^{-3} at fixed [neomenthol] $=5.0\times10^{-2}$ mol dm^{-3}, $[HClO_4]$ = 0.1 mol dm^{-3}, $[NaClO_4]$=0.4 mol dm^{-3}, ionic strength = 0.5 mol dm^{-3} in 70% (v/v) aqueous acetic acid at 313 Δ 0.1K in the presence of [mercuric acetate]$=1.0\times10^{-2}$ 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 the Table 2. The order in potassium bromate was established by initial rate method[16]. The plot of initial rate versus [potassium bromate] was a straight line passing through the origin showing thus the order in potassium bromate is one (Fig. 1). Subsequently pseudo first order plots were made since the concentration of neomenthol 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 rate constant (k_{obs}) were independent of the concentration of potassium bromate. (Fig 2). The empirical rate law at constant [H^+] and excess neomenthol concentration is

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

3.2 Neomenthol dependence: The dependence of the reaction rate on the concentration of neomenthol was studied by varying its concentration in the range 1.0 to 20.0×10^{-2} mol dm^{-3} at fixed [$KBrO_3$]=1.0×10^{-3} mol dm^{-3}, [$HClO_4$]=0.1 mol dm^{-3}, [$NaClO_4$] = 0.4 mol dm^{-3}, ionic strength = 0.5 mol dm^{-3}, in 70% (v/v) aqueous acetic acid at 313 ΔΔ0.1K 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 neomenthol was in excess, i.e. more than ten times the concentration of potassium bromate[13]. In each case good straight line was obtained (Fig 5.3). The plot of pseudo first order rate constant (k_{obs}) versus [neomenthol] is a straight line passing through the origin (Fig.5.4). It shows that the order of the reaction with respect to neomenthol is also one. The empirical rate law is, therefore,

$$-\frac{d[BrO_3^-]}{dt} = k_2[BrO_3^-][Neomenthol] \qquad \text{..... (3)}$$

where k_2 is second order rate constant and k_{obs} = k_2 [Neomenthol]. The pseudo first order rate constant (k_{obs}) values increased with an increase in [substrate]. The k_2 = k_{obs} / [substrate] values were also constant pointing to the fact that the order in [substrate] was also unity. The values of pseudo first order rate constant (k_{obs}) and second order rate constnat (k_2) under different experimental conditions are collected in Table 12.

The unit orders with respect to [$KBrO_3$] and [Neomenthol] 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/ [Neomenthol] (k_{obs} = pseudo first order rate constant) was linear passing through the origin (Fig. 5). This indicates the absence of complex formation or lack of kinetically detectable complex between potassium bromate and neomenthol in acidic medium.

3.3 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 [$KBrO_3$]=1.0×10^{-3} mol dm^{-3}, [Neomenthol] = 10.0×10^{-2} mol dm^{-3}, [$HClO_4$] = 0.1 mol dm^{-3}, [$NaClO_4$]=0.4 mol dm^{-3}, ionic strength 0.5 mol dm^{-3} in 70% (v/v) aqueous acetic acid at 313 Δ 0.1K[3]. The results of kinetic runs and the values of pseudo first order rate constants (k_{obs}) are given in Table 4. These results indicate that there is no significant effect of mercuric acetate concentration on the rate[6]. Thus the oxidation of neomenthol 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.

3.4 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 20.0×10^{-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}, [neomenthol] = 5.0×10^{-2} mol dm^{-3} in 70% (v/v) aqueous acetic acid at 313 Δ 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. The pseudo first order plots were made since the concentration of neomenthol was in excess, i.e. more than ten times the concentration of potassium bromate[5]. In each case good straight line was obtained (Fig 6). These results indicate that the rate depends nearly on the first power of [H^+] in the range of 0.05 to 0.15 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 0.20 mol dm^{-3}. Beyond 0.20 mol dm^{-3} of perchloric acid, the dissociation of potassium bromate is considerable, making further investigation on acid dependence difficult. Hence quantitative interpretation of acid dependence has not been attempted.

3.5 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 0.4 mol dm^{-3} at fixed [$KBrO_3$]=1.0×10^{-3} mol dm^{-3}, [neomenthol] =10.0×10^{-2} mol dm^{-3}, [$HClO_4$]=0.1 mol dm^{-3} in 70% (v/v) aqueous acetic acid at 313 Δ 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 6 These results indicate that there is no significant effect of ionic strength on the rate[8]. Thus the oxidation of neomenthol by potassium bromate is independent of ionic strength.

3.6 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_2O mixture in the range 40% to 90% (v/v) aqueous acetic acid at fixed [$KBrO_3$]= 1.0×10^{-3} mol dm^{-3}, [Neomenthol]= 10.0×10^{-2} mol dm^{-3}, [$HClO_4$]=0.1 mol dm^{-3}, [$NaClO_4$]=0.4 mol dm^{-3}, ionic strength = 0.5 mol dm^{-3} at 313 ΔΔ0.1K in the presence of

$[Hg(OAc)_2]$ = 1.0×10^{-2} mol dm^{-3}. The values of dielectric constant for various proportions of acetic acid have been reported earlier are used as such as shown in the Table 8. The results of kinetic runs and the values of pseudo first order rate constant (k_{obs}) are given in Table 7. These results indicate that the values of pseudo first order rate constant (k_{obs}) decrease as the percentage of acetic acid in AcOH: H_2O solvent mixture increases. Thus the reaction rate of the oxidation of neomenthol by potassium bromate decreases as the dielectric constant of the solvent mixture decreases[3]. The Amis plot of log k_2 versus 1/D and the Laidler-Eyring plot of log k_2 versus (D-1)/ (2D+1) are linear as shown in the Fig 7 and 8 respectively. It shows the dipole- dipole and ion-dipole interaction in the reaction.

3.7 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 temperatures dependence are tabulate in Table 9, 3 and 9 respectively. The values of pseudo first order rate constant (k_{obs}) and second order rate constant (k_2) at different temperature are collected in Table 12. These results indicate that the values of pseudo first order rate constant (k_{obs}) and second order rate constant (k_2) increases 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 in Table 10. The plot of log k_2 versus 1/T is shown in Fig. 9 which is linear showing that the Arrhenius equation relating to temperature with specific rate is followed[9]. 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), by different equations as described in chapter 2 and are tabulated in Table 11

3.8 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 diluting the reaction mixture with methanol, there was no formation of precipitate, indicating the absence of free radical intervention in the reaction[12]. The blank experiments of either neomenthol or potassium bromate with acrylonitrile alone did not induce polymerization under the same condition.

4. Discussion

The results obtained for the oxidation of neomenthol by potassium bromate in acidic medium is summarized as follows.

a) The reaction proceeds with a measurable velocity at 313 K.

b) The oxidation of neomenthol 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 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 showing thus the order in potassium bromate is one[16].

c) The oxidation of neomenthol by potassium bromate was found to follow first order kinetics with respect to neomenthol (substrate). The plot of pseudo first order rate constant (k_{obs}) versus [neomenthol] is a straight line passing through the origin. It indicates that the order of the reaction with respect to neomenthol is also one.
The unit orders with respect to $[KBrO_3]$ and [neomenthol] 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/ [neomenthol] (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 neomenthol in acidic medium.

d) There is no significant effect of mercuric acetate concentration on the rate of reaction. Thus the oxidation of neomenthol 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.

e) The results indicate that the rate depends nearly on the first power of $[H^+]$ in the range of 0.05 to 0.15 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 0.20 mol dm^{-3}. Beyond 0.20 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[17].

f) There is no significant effect of ionic strength on the rate of reaction. Thus the oxidation of neomenthol by potassium bromate is independent of ionic strength. Hence, the oxidation does not involve any reaction between ions.

g) The values of pseudo first order rate constant decreases as the percentage of acetic acid in AcOH: H_2O (solvent mixture) increases. Plots of log k_2 versus 1/D and log k_2 versus (D-1)/(2D+1) were found linear. This indicates dipole-dipole and ion-dipole interaction in the reaction.

h) 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	Energy of Activation (Ea)kJ mol^{-1}	Frequency factor 10^{-9} (A) mol^{-1} dm^3 sec^{-1}	Free energy of Activation (ΔG) kJ mol^{-1}	Entropy of Activation (ΔS) JK^{-1} mol^{-1}	Enthalpy of Activation (Δ kJ mol^{-1}
2.405	71.50	8.323	88.80	-63.73	68.86

There is no significant effect of ionic strength on the rate of reaction

i) The results indicate that one mole of potassium bromate is consumed for three moles of neomenthol in agreement with the following equation

$3C_9H_{18}CHOH + BrO_3^- \rightarrow 3C_9H_{18}CO + Br^- + 3H_2O$ ……..(1)

Neomenthol Menthone

j) The main product of oxidation of neomenthol with potassium bromate in acid perchlorate medium is menthone.

k) 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 of free radical mechanism in the oxidation of neomenthol with potassium bromate in acetic acid–perchloric acid medium.

Table 2 Variation of Potassium Bromate Concentration

10^3 [Hypo],M			30			60			120	
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	14.00	18.80	11.60	14.10	16.50	9.40	10.60	11.80	
5	8.55	12.90	17.40	10.60	13.00	15.10	8.65	9.70	10.90	
10	7.40	11.20	15.00	9.30	11.25	13.10	7.50	8.40	9.40	
15	6.40	9.60	13.20	8.00	9.70	11.55	6.60	7.40	8.20	
20	5.50	8.40	11.40	6.90	8.50	10.00	5.70	6.40	7.10	
25	4.70	7.50	9.80	5.90	7.40	8.50	4.90	5.50	6.10	
30	4.00	6.50	8.40	5.15	6.40	7.40	4.30	4.70	5.20	
10^7(-dc/dt)Ms^{-1}	5.00	7.20	9.60	12.00	14.50	16.80	18.90	21.50	24.00	
10^4 k_{obs} s^{-1}	5.00	4.64	4.81	4.93	4.73	4.78	4.68	4.84	4.87	

[Neomenthol] = 5.0×10^{-2}M $[HClO_4] = 10.0 \times 10^{-2}$M; $[NaClO_4] = 40 \times 10^{-2}$M; I = 50.0×10^{-2}M; Aliquot = 5 ml.; AcOH: H_2O = 70:30 $[Hg(OAc)_2] = 1.0 \times 10^{-2}$M; Temperature = 313K

Table3. Variation of Neomenthol Concentration

10^2 [Neomenthol],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	10.0	10.0	10.00	10.00	10.00	10.00	10.00	10.00	10.00
2	9.90	9.75	9.60	9.50	9.40	9.30	9.20	9.10	9.00	8.90
5	9.70	9.40	9.20	8.90	8.70	8.50	8.30	8.00	7.80	7.60
10	9.40	8.90	8.35	8.00	7.50	7.30	6.80	6.60	6.20	5.80
15	9.00	8.30	7.65	7.20	6.60	6.10	5.60	5.25	4.80	4.40
20	8.80	8.00	7.00	6.50	5.70	5.20	4.60	4.25	3.60	3.20
25	8.60	7.40	6.40	5.70	4.90	4.40	3.80	3.40	2.90	2.40
30	8.40	7.00	5.90	5.10	4.20	3.60	3.10	2.60	2.20	1.80
10^4 k_{obs} s^{-1}	0.98	1.98	2.94	3.74	4.80	5.67	6.50	7.48	8.40	9.52

$[KBrO_3] = 1.0 \times 10^{-3}$M $[HClO_4] = 10.0 \times 10^{-2}$M; $[NaClO_4] = 40 \times 10^{-2}$M I = 50.0×10^{-2}M; Aliquot = 5 ml. ; AcOH: H_2O = 70:30 $[Hg(OAc)_2] = 1.0 \times 10^{-2}$M; Temperature = 313K

Table 3 (Continued) Variation of Neomenthol Concentration

10^2[Neo-menthol]M	11.0	12.0	13.0	14.0	15.0	16.0	17.0	18.0	19.0	20.0
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	8.70	8.60	8.50	8.50	8.40	8.40	8.30	8.20	8.10	8.00
5	7.35	7.15	6.90	6.70	6.50	6.30	6.10	6.00	5.80	5.60
8	6.05	5.85	5.50	5.30	5.10	4.80	4.60	4.40	4.20	4.00
11	5.00	4.70	4.40	4.20	3.90	3.65	3.40	3.20	3.00	2.80
14	4.10	3.90	3.60	3.40	3.10	2.75	2.60	2.40	2.20	2.00
17	3.60	3.10	2.80	2.50	2.30	2.10	1.95	1.80	1.60	1.40
20	2.75	2.50	2.20	1.95	1.80	1.60	1.45	1.30	1.15	1.00
10^4 k_{obs} s^{-1}	10.75	11.54	12.60	13.60	14.30	15.27	16.18	16.98	18.00	19.16

$[KBrO_3] = 1.0 \times 10^{-3}$M $[HClO_4] = 10.0 \times 10^{-2}$M; $[NaClO_4] = 40 \times 10^{-2}$M; I = 50.0×10^{-2}M; Aliquot = 5 ml.; AcOH: H_2O = 70:30; $[Hg(OAc)_2] = 1.0 \times 10^{-2}$M; Temperature = 313K

Table 4 variation of Mercuric acetate concentration

10^2[Hg(OAc)$_2$],M	1.0	2.0	3.0	4.0	5.0
Time in minutes	Volume in ml. of 3.0×10^{-3}M Hypo				
0	10.00	10.00	10.00	10.00	10.00
2	8.90	8.90	9.00	9.00	8.90
5	7.60	7.60	7.70	7.60	7.60
10	5.80	5.80	5.85	5.85	5.80
15	4.40	4.35	4.50	4.50	4.40
20	3.40	3.30	3.45	3.50	3.40
25	2.60	2.50	2.65	2.70	2.60
30	1.80	1.70	1.85	1.90	1.80
10^4 k_{obs} s^{-1}	9.52	9.80	9.40	9.25	9.52

[$KBrO_3$] = 1.0×10^{-3}M; [Neomenthol] = 10.0×10^{-2}M; [$HClO_4$]=10.0×10^{-2}M; [$NaClO_4$] = 40.0×10^{-2}M; I = 50.0×10^{-2}M; Aliquot = 5 ml.; AcOH: H_2O = 70:30; Temperature = 313K

Table 5.5 Variation of hydrogen ion concentration

10^2[$HClO_4$]M	5.0	10.0	15.0	20.0
10^2 [$NaClO_4$]M	45.0	40.0	35.0	30.0
Time in minutes	Volume in ml. of 3.0 × 10^{-3}M Hypo			
0	10.00	10.00	10.00	10.00
2	9.70	9.40	9.10	8.75
5	9.30	8.70	8.00	7.35
10	8.70	7.50	6.60	5.20
15	8.20	6.60	5.40	3.80
20	7.50	5.70	4.40	2.75
25	7.10	4.90	3.50	2.05
30	6.60	4.20	2.70	1.40
10^4 k_{obs} , s^{-1}	2.40	4.80	7.20	11.00

[$KBrO_3$]=1.0×10^{-3}M; [Neomenthol] = 5.0×10^{-2}M; [$Hg(OAc)_2$]= 10.0×10^{-2}M; Aliquot = 5 ml.; I = 50.0 × 10^{-2}M; AcOH: H_2O = 70:30; Temperature = 313K

Table 6 Variation of ionic strength with Sodium perchlorate

10^2[$NaClO_4$]M	0.0	10.0	20.0	30.0	40.0
Time in minutes	Volume in ml. of 3.0 × 10^{-3}M Hypo				
0	10.00	10.00	10.00	10.00	10.00
2	9.00	8.90	8.90	9.00	8.90
5	7.70	7.60	7.60	7.60	7.60
10	5.85	5.80	5.80	5.85	5.80
15	4.50	4.40	4.35	4.50	4.40
20	3.45	3.40	3.30	3.50	3.40
25	2.65	2.60	2.50	2.70	2.60
30	1.85	1.80	1.70	1.90	1.80
10^4 k_{obs} s^{-1}	9.40	9.52	9.80	9.25	9.52

[$KBrO_3$] = 1.0×10^{-3}M; [Neomenthol] = 10.0×10^{-2}M; [$HClO_4$] = 10.0×10^{-2}M; Aliquot = 5 ml.; [$Hg(OAc)_2$] = 1.0 × 10^{-2}M; AcOH: H_2O = 70:30; Temperature = 313K

Table 5.7 Variation of dielectric constant

AcOH: H_2O	40:60	50:50	60:40	70:30	80:20	90:10
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
2	8.60	8.75	8.85	8.90	9.00	9.20
5	7.10	7.35	7.45	7.60	7.80	8.30
10	5.00	5.20	5.50	5.90	6.20	6.80
15	3.50	3.80	4.20	4.50	4.80	5.60
20	2.40	2.70	3.00	3.40	3.60	4.60
25	1.70	2.00	2.30	2.60	2.90	3.80
30	1.20	1.40	1.60	1.80	2.20	3.10
10^4 k_{obs} s^{-1}	11.70	10.92	10.20	9.52	8.40	6.50

[$KBrO_3$] = 1.0×10^{-3}M; [Neomenthol] = 10.0×10^{-2}M; [$HClO_4$]= 10.0×10^{-2}M; [$NaClO_4$] = 40.0×10^{-2}M; Aliquot = 5 ml.; I = 50.0×10^{-2}M; [$Hg(OAc)_2$] = 1.0×10^{-2}M; Temperature = 313K

Table 8

AcOH: H_2O	D	$10^2 \times (1/D)$	(D-1)/(2D+1)	$10^3\ k_2\ M^{-1}s^{-1}$	3+logk_2
40:60	48.70	2.053	0.4848	11.70	1.0682
50:50	41.40	2.415	0.4821	10.92	1.0382
60:40	34.00	2.941	0.4783	10.20	1.0086
70:30	27.90	3.584	0.4736	9.52	0.9786
80:20	20.30	4.926	0.4639	8.40	0.9242
90:10	14.10	7.092	0.4486	6.50	0.8129

Table 9 Variation of Neomenthol concentration

Temperature	303				323			
102[Neomenthol], M	4.0	6.0	8.0	10.0	1.0	2.0	3.0	4.0
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
2	9.80	9.70	9.60	9.50	9.70	9.40	9.15	8.90
5	9.45	9.30	9.10	8.85	9.30	8.70	8.25	7.60
10	9.00	8.75	8.20	7.85	8.75	7.65	6.80	5.90
15	8.60	8.25	7.60	6.80	8.25	6.60	5.60	4.50
20	8.20	7.50	6.90	6.10	7.50	5.80	4.40	3.30
25	7.80	7.10	6.30	5.40	7.10	5.10	3.60	2.60
30	7.50	6.50	5.70	4.80	6.50	4.50	2.90	1.90
$10^4\ k_{obs}$,s^{-1}	1.65	2.40	3.12	4.12	2.40	4.50	6.88	9.25

$[KBrO_3]$ = 1.0 × 10^{-3}M; [$HClO_4$] = 10.0 × 10^{-2}M; $[NaClO_4]$ = 40.0 × 10^{-2}M; I = 50.0 ×10^{-2}M; Aliquot = 5 ml.; AcOH: H_2O = 70:30 $Hg(OAc)_2$] = 1.0×10^{-2}M; Temperature = 313K

Table 10: The values of temperature (T) reciprocal of temperature (1/T), second order rate constant (k_2) and log k_2

Temperature K	$10^3 \times (1/T)$	$10^3\ k_2\ M^{-1}\ s^{-1}$	3 + log k_2
303	3.300	4.00	0.6021
313	3.195	9.58	0.9814
323	3.096	23.10	1.3636

Table 11: 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)

Temperature K	$10^3\ k_2$ $M^{-1}\ s^{-1}$	Temperature Coefficient	(Ea)	10^{-9} (A)	(ΔG)	(ΔS)	(ΔH)
303	4.00	----	-----	8.424	88.17	-63.36	---
313	9.58	2.395	68.88	8.149	88.80	-63.90	66.28
323	23.10	2.415	74.12	8.395	89.44	-63.92	71.44
Average		2.405	71.50	8.323	88.80	-63.73	68.86

5. Conclusion

During the study of kinetics and mechanism of neomenthol in acidic medium by potassium bromate, it is concluded that the reaction proceeds with a measurable velocity at 313 K. The oxidation of neomenthol by potassium bromate was found to follow first order kinetics with respect to potassium bromate (oxidant). The results indicate that the rate depends nearly on the first power of $[H^+]$ in the range of 0.05 to 0.15 mol dm^{-3} but exhibit higher order dependence on $[H^+]$ at higher [acid] at constant ionic strength. There is no significant effect of ionic strength on the rate of reaction. The results indicate that one mole of potassium bromate is consumed for three moles of neomenthol in agreement with the following equation-

$$3C_9H_{18}CHOH + BrO_3^- \rightarrow 3C_9H_{18}CO + Br^- + 3H_2O \quad \text{.....(1)}$$

Neomenthol Menthone

The main product of oxidation of neomenthol with potassium bromate in acid perchlorate medium is menthone.

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