



Kinetics and Mechanism of Oxidation of Guaifenesin by Keggin type 12-Tungstocobaltate (III) in Hydrochloric Acid

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Abstract

The kinetics of oxidation of expectorant drug guaifenesin by 12-tungstocobaltate (III) was studied spectrophotometrically at λ_{max} 624 nm under pseudo first-order conditions in aqueous acidic medium at a constant ionic strength of 0.3 mol dm⁻³. The stoichiometry of the reaction was found to be 1 : 2, [Guaifenesin : 12-tungstocobaltate (III)] in acidic medium. The products of the reaction were identified by using spectral studies, FT-IR, ¹H-NMR, and mass. The effect of [H⁺] ion and ionic strength on the rate of reaction have been investigated. The rate constants for slow steps of the mechanism are calculated. The values of activation parameters have been evaluated by using the plots log k versus 1/T and log(k/T) versus 1/T. By using the observed results the mechanism of the reaction has been proposed.

Keywords: Mechanism, Keggin type 12-tungstocobaltate(III), Oxidation, Guafenesin.

Introduction

Due to their high thermal stability strong acidity and strong oxidizing ability, heteropolyacids (HPAs) are widely used as homogeneous and heterogeneous catalyst¹. Many polyoxometalates exhibit significant biological activity². In 1971 Raynaud et al have reported the antiviral activity of polyoxometalates³. Further studies by various researchers showed the effectiveness of these polyoxometalates against several viruses such as stomatitis, vesicular, rubella, rauscher leukemia, rabies, polio etc.³. Baker and co-workers⁴ have firstly synthesized, characterized the [Co^{III}W₁₂O₄₀]⁵⁻ and it has been extensively used as an oxidant both for inorganic and organic substrates⁵. [Co^{III}W₁₂O₄₀]⁵⁻ has been reported as a well defined probe for determining the nature of outer-sphere oxidations of alkyl aromatic hydrocarbons⁶. The complex of transition metal ions with polyoxoanions like polytungstates have been extensively used as an outer-sphere electron transfer reagent⁷. The redox reaction of [Co^{III}W₁₂O₄₀]⁵⁻ have been recently reviewed^{4,5}. Out of various heteropolyacids, the Keggin type heteropolyacids have been widely used as heterogeneous and homogeneous catalysts for oxidation and acid-base reactions⁸.

Guaifenesin is a propanediol derivative which is also known as glycercyl guaiacolate (3-(2-methoxyphenoxy) 1,2-propanediol). Guaifenesin is an expectorant drug, usually taken orally to assist the expectoration of phlegm from the airways in acute respiratory tract infections⁹. Guaifenesin is prone to act as an expectorant by increasing the volume and reducing the viscosity of secretions in the trachea and bronchi. It assists in the flow of respiratory tract secretions and allows ciliary movement to carry the loosened secretions upward toward the pharynx¹⁰. The

guaifenesin is the principal drug used in the treatment of coughing. A cochrane collaboration meta-analysis of different medicines for acute cough in children and adults revealed that there was insufficient high-quality clinical data to attest or disprove the efficiency of examined drug like guaifenesin¹¹. It is also useful in relief of tremors of Parkinsonism acute alcoholism, anxiety and tension. Guaifenesin is used alone for its sedative action in anxiety and tension states¹². It is most often used in combination with antihistamines, analgesics and vasoconstrictors in cough medicines for its expectorant action one of the derivatives of guaifenesin is methocarbamol, which is widely used for the relief of skeletal muscle spasms¹². The present paper reports the kinetic of oxidation of guaifenesin by [Co^{III}W₁₂O₄₀]⁵⁻ in acid medium with a view to investigate the mechanism of this drug in solution.

Materials and Methods

All chemicals used were of analytical reagent grade and double distilled water was used throughout the work. A solution of guaifenesin was prepared by dissolving a known amount of recrystallized sample in double distilled water. The purity of guaifenesin sample was checked by comparing its IR spectrum and melting point (80°C) with literature data. The cobalt complexes [Co^{III}W₁₂O₄₀]⁵⁻ and [Co^{II}W₁₂O₄₀]⁶⁻ were prepared by the reported method¹³⁻¹⁵. The ionic strength was maintained using NaClO₄ (BDH) and HCl (BDH) was used to vary the hydrogen ion concentration.

Kinetic studies: The kinetic measurements were performed on a ShimadzuUV-1800-UV-Visible spectrophotometer. The kinetics was followed under pseudo first-order conditions where

guaifenesin was always taken in excess over $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ at a constant ionic strength of 0.3 mol dm^{-3} in acidic medium at constant temperature $27 \pm 0.2^\circ\text{C}$. The reaction was initiated by mixing the $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and guaifenesin solutions, which also contains requisite concentration of HCl and NaClO_4 . The reaction was monitored by measuring the absorbance of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ at 624 nm as a function of time. Beer's law was tested for $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ between the concentration of 1.0×10^{-3} and $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ($\epsilon_{624} = 180 \pm 2 \text{ mol dm}^{-3} \text{ cm}^{-1}$)¹⁶ under the experimental conditions. The pseudo first-order rate constants, were obtained from the plot of $\log [\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ versus time. The rate constants were reproducible within $\pm 10\%$.

Spectrophotometric measurement: The UV-Visible spectra of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ complex and the reaction mixture were recorded by using ShimadzuUV-1800-UV-Visible spectrophotometer between the wavelength range 480-720 nm. The spectra of the

reaction mixture at various time intervals are shown in (Figure-1).

Results and Discussion

Stoichiometry and product Analysis: Five different sets of reaction mixtures containing different concentrations of guaifenesin and $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ in presence of 0.5 mol dm^{-3} HCl were equilibrated at $27 \pm 0.2^\circ\text{C}$ for 24 hours in a nitrogen atmosphere. The progress of the reaction was monitored by measuring the absorbance at 624 nm for the formation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$. The results revealed that the two moles of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ consumes one mole of guaifenesin.

The reaction product, 2-methoxy phenoxy acetic acid was extracted with ethyl acetate and recrystallized from aqueous alcohol. The product was identified as 2-methoxy phenoxy acetic acid by its melting point $118\text{-}122^\circ\text{C}$, IR Spectrum (KBr), $^1\text{H-NMR}$ spectrum (Figure-2) and the mass spectrum.

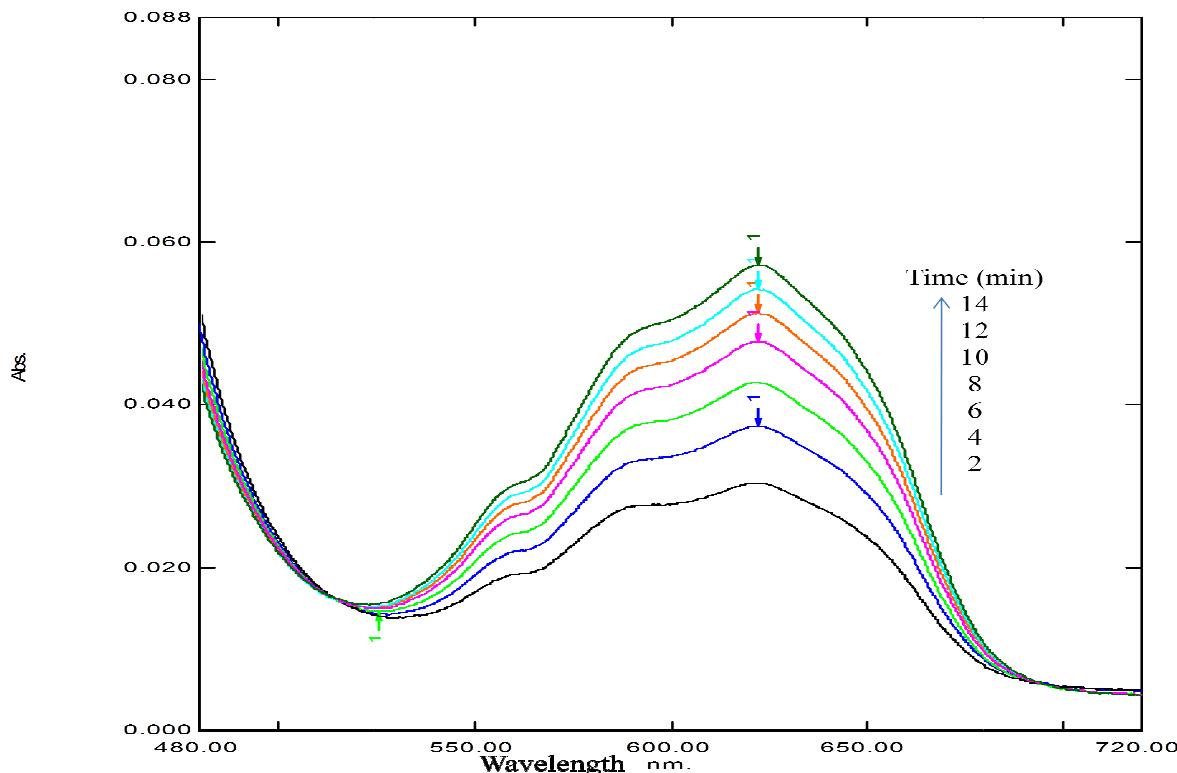
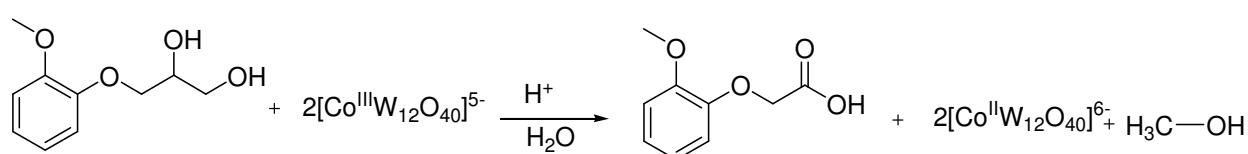


Figure-1
Spectra of the reaction mixture at different time intervals at $27 \pm 0.2^\circ\text{C}$, $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-} = 0.1 \times 10^{-3} \text{ mol dm}^{-3}$, [guaifenesin] = $0.3 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{HCl}] = 0.5 \text{ mol dm}^{-3}$, $[\text{NaClO}_4] = 0.3 \text{ mol dm}^{-3}$.



Scheme-1

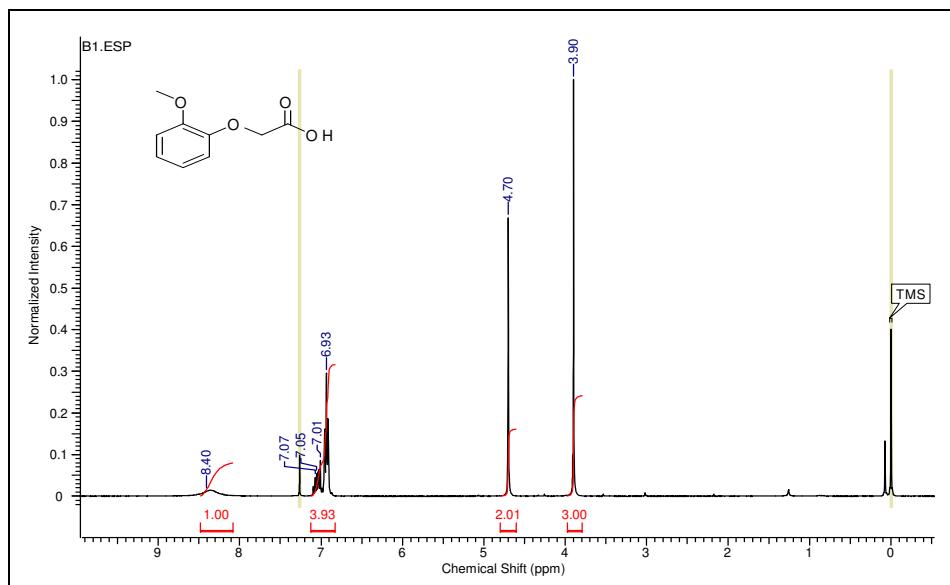


Figure-2
NMR spectrum of the product of reaction

Reaction order: The reaction orders have been determined from the slopes of $\log k_{\text{obs}}$ versus log (concentration) plots by varying the concentration of guaifenesin, $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and HCl in turn while keeping other constant. The concentration of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ was varied in the range 1.5×10^{-3} to 3.5×10^{-3} mol dm $^{-3}$ at fixed [guaifenesin], $[\text{H}^+]$ and ionic strength. The constancy in the pseudo first order rate constant at various concentrations of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ indicates the order in $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ as unity (Table-1). The guaifenesin concentration was varied in the range 1.0×10^{-2} to 5.0×10^{-2} mol dm $^{-3}$ at $27 \pm 0.2^\circ\text{C}$ keeping all other reactants concentration and conditions constant. The order in guaifenesin was found to be near to unity (0.80) under the experimental conditions. The effect of concentration of acid on the reaction rate was studied by keeping [guaifenesin], $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ and ionic strength constant. The rate constants were found to be enhanced with increasing the acid concentration and the order in $[\text{H}^+]$ was found to be unity (Table-1).

Effect of hydrogen ion concentration: The effect of $[\text{H}^+]$ on the rate of reaction was studied by varying the $[\text{H}^+]$ from 0.01 to 0.5 mol dm $^{-3}$ by keeping constant [guaifenesin] and $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ at ionic strength 0.3 mol dm $^{-3}$ and temperature $27 \pm 0.2^\circ\text{C}$. With increase in $[\text{H}^+]$, the reaction rate increases (Table-1) indicating the protonation¹⁷ of the guaifenesin under the experimental condition. The order in $[\text{H}^+]$ was found to be unity as determined from the plot of $\log k_{\text{obs}}$ against $\log [\text{H}^+]$.

Effect of ionic strength: The effect of ionic strength was studied by using sodium perchlorate within 0.1 to 1.2 mol dm $^{-3}$, by keeping reactant concentrations and other conditions constant. It was found that the rate of reaction increases with increasing the ionic strength¹⁸. The plot of $\log k_{\text{obs}}$ versus $I^{1/2}$ shows linearity with positive slope.

Table-1
Effect of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$, [Guaifenesin], $[\text{H}^+]$ for the oxidation of guaifenesin by $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ in acidic medium at $27 \pm 0.2^\circ\text{C}$, $I = 0.3 \text{ mol dm}^{-3}$.

$[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ 10^{-3}	[Guaifenesin] 10^2	[HCl]	$k_{\text{obs}} 10^3$
1.5	2.0	0.1	2.3
2.0	2.0	0.1	2.3
2.5	2.0	0.1	2.3
3.0	2.0	0.1	2.3
3.5	2.0	0.1	2.3
2.0	1.0	0.1	1.8
2.0	2.0	0.1	2.3
2.0	3.0	0.1	4.6
2.0	4.0	0.1	6.9
2.0	5.0	0.1	9.2
2.0	2.0	0.1	2.3
2.0	2.0	0.2	4.6
2.0	2.0	0.3	6.9
2.0	2.0	0.4	9.2
2.0	2.0	0.5	11.5

Effect of solvent polarity: The relative permittivity effect was studied by varying the percentage of acetonitrile from 0 to 40 % v/v in the reaction mixture by keeping all other conditions constant. The relative permittivities of the reactions mixtures were determined from the values of the pure solvents. It was found that the rate constant of the reactions were unaffected by changing solvent polarity¹⁹.

Test for free radicals: To understand the intervention of free radicals, the reaction was studied in presence of added acrylonitrile^{20,21}. The acrylonitrile, free radical scavenger was added to the reaction mixture and it was kept for 24 hours under nitrogen atmosphere. After 24 hours the reaction mixture was diluted with methanol, formation of white precipitate of polymer indicates the involvement of free radicals in the reaction²².

Effect of temperature: The effect of temperature on the reaction was studied by performing the experiment at four different temperatures at 293, 303, 308, and 313 K by keeping all other conditions constant. The rate constants were found to increase with increase in temperature (Table-2). The activation parameters of the reaction were evaluated from the Arrhenius and Eyring plots of $\log k_{\text{obs}}$ versus. (1/T) and $\log (k_{\text{obs}}/T)$ versus 1/T. The activation parameters were found to be $E_a = 84.85 \text{ kJ mol}^{-1}$, $\Delta H^\# = 82.33 + 5 \text{ kJ mol}^{-1}$, $\Delta G^\# = 86.73 + 6 \text{ kJ mol}^{-1}$ and $\Delta S^\# = -14.51 + 5 \text{ J K}^{-1} \text{ mol}^{-1}$

Table-2

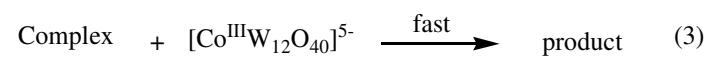
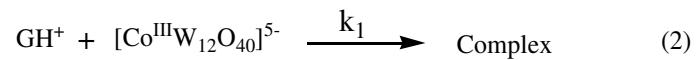
Effect of temperature on rate for the oxidation of guaifenesin by $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ in aqueous acidic medium

Temperature K	$10^2 k_{\text{obs}} \text{ s}^{-1}$
293	1.11
298	2.30
303	4.60
308	6.90
313	9.21

Discussion: The oxidation of guaifenesin by the Co(III) complex²³ proceeds with two single-electron transfer steps. By considering the kinetics of electron exchange between Co(II) and Co(III) using ⁶⁰Co tracer techniques along with structure and stability of these anions it appears that the tungstate groups are substitutionally inert and therefore it was widely used as an outer-sphere electron transfer reagents²⁴.

The reaction between guaifenesin (G) and $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ in acidic medium shows stoichiometry of 1:2 with an order of unity for both guaifenesin acid and guaifenesin. First order dependence on $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ concentration has been observed

during the reaction. The added products do not affect the rate of reaction. By considering the observed results, following mechanism has been proposed and given in Scheme-2.



Scheme-2

Protonation of guaifenesin takes place under the experimental condition. The protonated guaifenesin species and unprotonated $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ are the active species in the reaction which led to complex (C) in slow step. The complex (C) then reacts with second molecule of $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ in fast step to give the product.

$$\text{Rate} = \frac{K_1 k_1 [\text{Guaifenesin}]_T [\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}}{(K_1 + [\text{H}^+])} \quad (4)$$

$$k_{\text{obs}} = \frac{K_1 k_1 [\text{Guaifenesin}]_T}{(K_1 + [\text{H}^+])} \quad (5)$$

The reaction gives 2-methoxy phenoxy acetic acid as a main product. The product was identified by using IR Spectrum (KBr), which showed a band at 1710 cm^{-1} due to $>\text{C=O}$ stretching of acid and a broad band at 3410 cm^{-1} due to -OH stretching and aromatic C=C stretching of 1589 cm^{-1} . It was further characterised by the ¹H-NMR spectrum shows peaks δ 6.93-7.07 (m, 4H), 4.70 (s, 2H), 3.90 (s, 3H), and 8.40 (s 1H, carboxylic -OH), respectively. The mass spectra showed a (M^+) molecular ion peak at 182 amu, conformed the presence of 2-methoxy phenoxy acetic acid.

Kinetics of oxidation of guaifenesin was investigated at several initial concentrations of reactants in acidic medium. The oxidant $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ concentration was varied from $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ to $3.5 \times 10^{-3} \text{ mol dm}^{-3}$ by keeping constant [guaiifenesin], [HCl] and $[\text{NaClO}_4]$ at $27 \pm 0.2^\circ\text{C}$. The constancy in observed rate constants k_{obs} (Table 1) indicate that the order with respect to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ was found to be unity which was further supported by linearity of the plot $\log [\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ versus time. Similarly, on varying the [guaiifenesin] and by keeping all other conditions constant, the order with respect to guaifenesin was found to be unity.

The effect of ionic strength and solvent polarity was studied by keeping $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ [guaifenesin] and [HCl] at $2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ and 0.1 mol dm^{-3} . Sodium perchlorate and acetonitrile were used to vary the ionic strength and the solvent polarity respectively. The rate of the reaction increases with increase in ionic strength and remains unchanged with change in solvent polarity.

The effect of temperature on the rate of the reaction was studied by carrying out the reaction at four different temperatures 25, 30, 35 and 40°C. The pseudo first order rate constants thus obtained are tabulated in (Table-2). The plot of $\log k_{obs}$ versus $1/T$ was found to be linear showing that the reaction obeys Arrhenius temperature dependence. The values of enthalpy of reaction (ΔH), entropy of reaction (ΔS) and free energy of activation (ΔG) were calculated as 82.33 kJ mol⁻¹, -14.51 J K⁻¹ mol⁻¹ and 83.73 kJ mol⁻¹ respectively. The values of activation parameters are in agreement with the proposed mechanism.

Conclusion

The reaction between guaifenesin and $[Co^{III}W_{12}O_{40}]^{5-}$ in hydrochloric acid was carried out under pseudo-first-order conditions keeping excess of guaifenesin. 2-methoxy phenoxy acetic acid was to be the product of the reaction. The unprotonated $[Co^{III}W_{12}O_{40}]^{5-}$ and protonated guaifenesin were found to be reactive species under the reaction conditions. The reaction proceeds with formation of complex between the active forms of the reactants in slow step. The free radical intervention was detected in the reaction since the added acrylonitrile form precipitate and affects the rate of the reaction. A mechanism involving slow complex formation and subsequent reaction of this complex with second molecule of the oxidant in fast step to give the products has been proposed.

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