



Kinetics of Oxidation of Atropine by Alkaline KMnO_4 in Aqueous Solutions

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Kinetics of oxidation of atropine by alkaline KMnO_4 has been studied in aqueous solutions at various temperatures. Kinetic measurements were performed at constant pH and constant ionic strength, under pseudo-first order condition in which the concentration of atropine was around an order of magnitude greater than that of KMnO_4 . The observed rate constant was obtained by following the change in absorbance of the reaction mixture with time at a predetermined wavelength. The overall rate constant and the orders of the reaction with respect to concentrations of both atropine and KMnO_4 were determined. Two observed rates and hence, two rates constant were found. This indicates that the oxidation process occurs in two steps with the formation of intermediates. A suggested mechanism for the reaction is given which agrees with kinetics results. The activation energy of the process was convoluted from temperature effect on the rate of the reaction.

Keywords: Kinetics, Atropine, Potassium permanganate, Anticholinergic.

INTRODUCTION

Atropine sulfate monohydrate (ASM, Fig. 1) is pharmaceutical formulation that is one of the World Health Organization's list of essential medicines¹. Atropine itself is a naturally occurring tropane alkaloid with chemical structure similar to that of cocaine. Plants of the family Solanaceae that includes *Atropa belladonna*, *Datura stramonium* and *Mandragora officinarum* are the major natural sources of the alkaloid. Atropine serves as a drug with a wide variety of effects². It is a competitive antagonist of the muscarinic acetylcholine receptors, hence its major effects are on the parasympathetic nervous system. As an anticholinergic drug (parasympatholytic) it is considered a nonselective muscarinic acetylcholinergic antagonist. Consequently, its main medical uses are based on these potent biological properties. Since it blocks the action of the vagus nerve, atropine is used in resuscitation procedures³. Additionally, atropine mixed with pralidoxime chloride (2-PAM chloride) is used as an antidote for poisoning by organophosphate insecticides and nerve gases, such as Tabun (GA), Sarin (GB), Soman (GD) and VX⁴. Atropine has also several medical applications that include ophthalmic uses as therapeutic mydriatic and in slowing the progression of myopia in children^{5,6}.

As much as it is crucially important to understand this kind of physiological activity⁷, atropine interactions with common chemical reagents are still lacking. Oxidation of atropine by

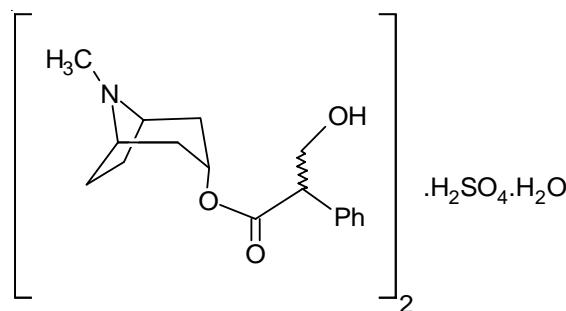


Fig. 1. Chemical structure of atropine sulfate monohydrate

alkaline copper(III) periodate complex has been recently reported^{8,9}. Organic oxidation protocols have commonly employed transition metal complexes in their higher oxidation states that can be stabilized by appropriate polydentate ligands^{10,11}. Atropine oxidation by typical strong oxidizing reagents including potassium dichromate and potassium permanganate in appropriate pH media have never been reported to the best of our knowledge. Understanding the behaviour of atropine when treated with powerful oxidizing agents in aqueous media might shed some light into its interaction with oxidative enzymes such as FAD and NADP¹².

Kinetics of oxidation of organic substrates by alkaline KMnO_4 has been reported in literature and demonstrated to be a powerful mechanism elucidating tool. Examples include oxidation of DL-aspartic acid and sugars^{13,14}.

It is assumed that, under the reaction conditions and stoichiometries used herein, oxidation of the aliphatic alcohol of atropine to a carboxyl group is the predominant reaction¹⁵ (**Scheme-I**). Permanganate ion attains its optimum stability in neutral to slightly alkaline media¹⁶. However, in strongly alkaline media, it disproportionates to manganese(V) (hypomanganate) or manganese(VI) (manganate). Hence, for oxidation reactions under these conditions it will be difficult to determine whether a one or two electron process is operating¹². To sort out the exact reaction of basic KMnO_4 with atropine a set of preliminary experiments were done.

In the present work, as an extension of our previous studies¹⁷⁻²⁰ on both kinetics and biological application to widen our knowledge about the oxidation of biologically important substances, we report the kinetics of oxidation of atropine by alkaline KMnO_4 . Kinetic results at various temperatures are presented and a proposed mechanism for the oxidation process is given and discussed.

EXPERIMENTAL

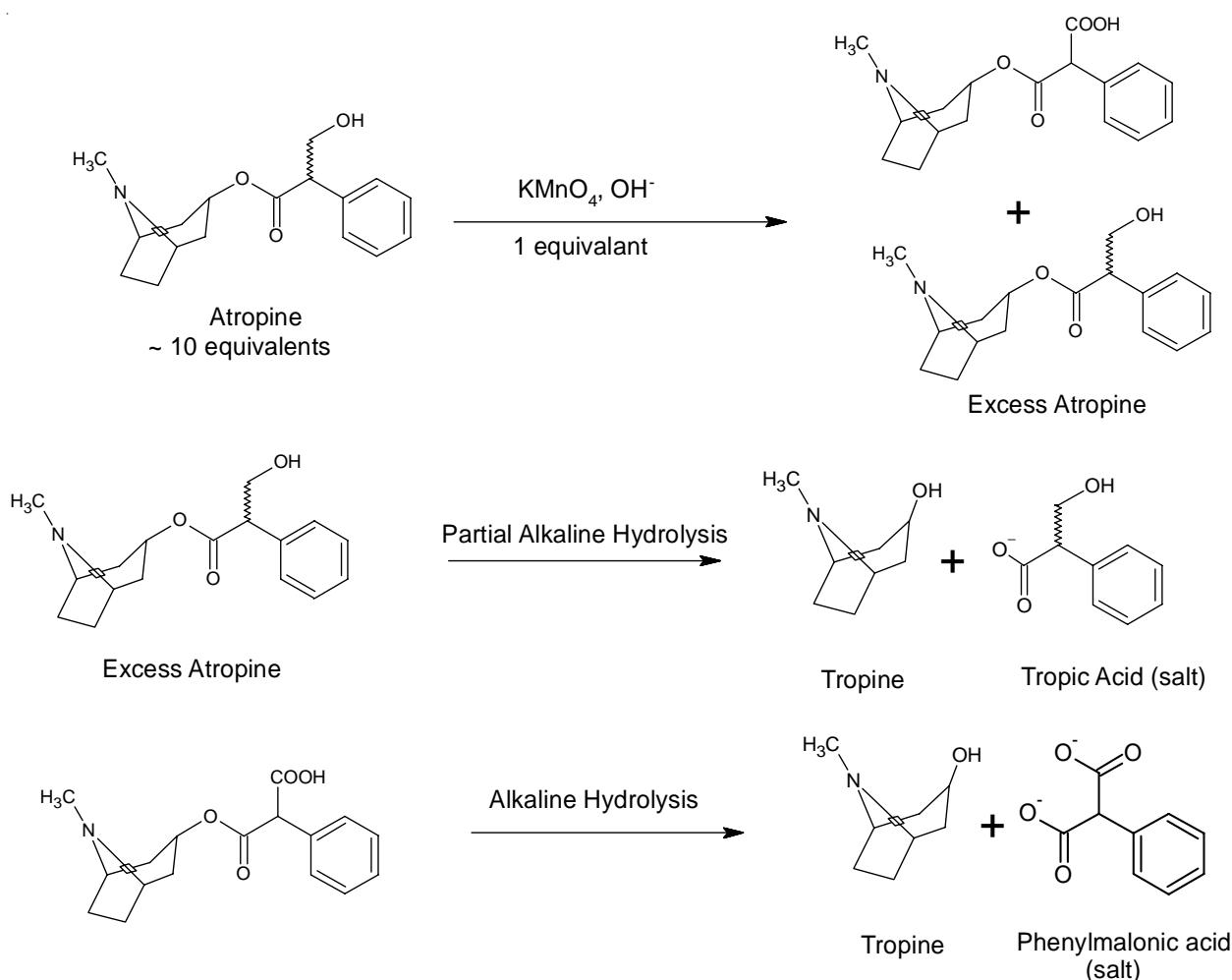
Alkaline hydrolysis: Atropine sulfate monohydrate (0.10 M) was treated with KOH (1.0 M) solution for 25 min (optimum run time frame for reaction monitoring, arbitrary set). Hydrolysis products were then isolated, purified and characterized by NMR and IR spectroscopy. Results indicated that hydrolysis

did not proceed to any measurable extent. However, the addition of MnO_2 greatly enhanced the hydrolysis.

Alkaline KMnO_4 disproportionation: A blank run of mixing all ingredients [KMnO_4 (0.001 M), KOH 0.10 M)] except atropine sulfate monohydrate has shown that the change in absorption by KMnO_4 is negligible throughout the measuring period.

Alkaline KMnO_4 oxidation: Atropine sulfate monohydrate solution (0.01 M) (about 10 folds in excess) was treated with the alkaline KMnO_4 (0.001 M) solution for 25 min. Products were isolated, purified and thoroughly characterized. The products were excess atropine, tropine, tropic acid and phenylmalonic acid (**Scheme-I**). Addition of mercuric chloride or acrylonitrile monomer to the reaction system, directly after the appearance of the green colour of MnO_4^{2-} , induced a white precipitate formation and polymerization, respectively. Consequently, a radical formation throughout the course of the reaction mechanism cannot be ruled out^{21,22}. The reaction was quenched and the green colour persists.

These results implicated that the major change in the oxidant concentration (absorbance at its maximum wavelength) is attributed to the oxidation of atropine primary alcohol. Hence, kinetic measurements were designed to follow up this reaction. It is aimed to investigate the mechanism by which the reaction is taking place.



Scheme-I: Main reactions of atropine in presence of KMnO_4 in basic medium

Kinetics measurements: Freshly prepared aqueous solutions of desired concentrations of atropine sulfate monohydrate and KMnO_4 were used in the kinetic study. In a strongly basic solution (0.1 M), atropine sulfate monohydrate is converted to atropine. Measurements were carried out using a Diode Array Spectrophotometer model 8453E from HP Agilent Technologies. Reactions were monitored by following the change in absorbance of (MnO_4^{2-}) reaction mixture with time at a predetermined wavelength. The wavelength was determined by recording the absorption spectra for KMnO_4 alone and for its mixture with atropine sulfate monohydrate after completion of the reaction. The wavelength of maximum absorbance difference (λ_{max}), preferably in visible region of the spectra, between the absorption of KMnO_4 and the reaction mixture was selected. A λ scan for reactants and products at various time intervals is shown in Fig. 2, from which $\lambda_{\text{max}} = 440 \text{ nm}$ was selected. At this wavelength absorbance is mainly due to MnO_4^{2-} and absorbance due to all other Mn species is minimal. Also, it should be noted that none of the organic compounds, reactants or products, absorb at this wavelength.

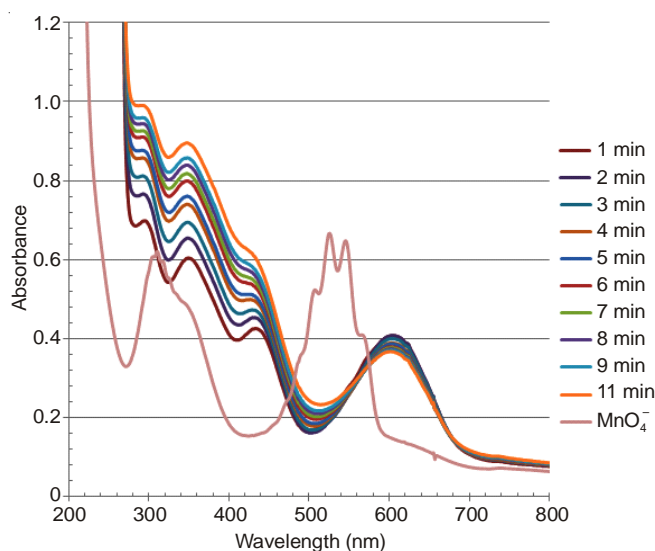
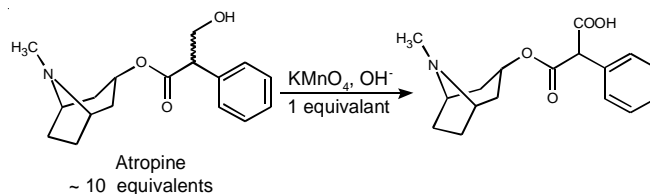


Fig. 2. Plot of absorbance vs. λ for the product and for the reactant of the oxidation of atropine by MnO_4^{2-} . Kinetic experiment was studied at $\lambda_{\text{max}} = 440 \text{ nm}$

All reactions were studied under pseudo-first order conditions, at which the concentrations of atropine sulfate monohydrate [10^{-2} to $10^{-1} \text{ mol dm}^{-3}$] were at least an order of magnitude larger than those of KMnO_4 [10^{-4} to $10^{-2} \text{ mol dm}^{-3}$]. The pH of the reaction mixture was maintained constant at 13.0 ± 0.1 and its ionic strength was fixed using NaClO_4 . Rates were measured at various temperatures and for each measurement it was maintained constant within $\pm 0.1 \text{ }^\circ\text{C}$.

RESULTS AND DISCUSSION

The main reactions of oxidation of atropine by KMnO_4 in basic medium are shown in **Scheme-I**. Since kinetics measurements were run under pseudo first order condition, in which the concentration of atropine is an order of magnitude larger than that for KMnO_4 , then, the first stage of the process which involves the oxidation of atropine by alkaline KMnO_4 is given by the following equation:



An excess of atropine remains. The excess atropine is expected to undergo partial hydrolysis due to the presence of MnO_2 as byproduct which acts as an auto-catalyst to give tropine and tropic acid and the oxidized product in stage I is also expected to undergo an alkaline hydrolysis to yield tropine and phenylmalonic acid (**Scheme-I**). The rate of oxidation of atropine is given by:

$$\text{Rate} = k[\text{ATN}]^a[\text{KMnO}_4]^b \quad (1)$$

where k is the reaction rate constant and a & b are orders of reaction with respect to concentrations of atropine and KMnO_4 , respectively. The concentration of OH^- was kept constant at 0.10 M throughout the all kinetics measurements. Under pseudo-first order conditions in which $[\text{ATN}] \gg [\text{KMnO}_4]$, the concentration of atropine is essentially constant throughout the reaction. The reaction rate is thus given by:

$$\text{Rate} \approx -\frac{d[\text{KMnO}_4]}{dt} = k_{\text{obs}}[\text{KMnO}_4]^b \quad (2)$$

where k_{obs} is the observed rate for reaction is given by:

$$k_{\text{obs}} = k[\text{ATN}]^a \quad (3)$$

where k is the rate constant for eqn. 1.

For a first-order dependence of reaction rate on $[\text{KMnO}_4]$, experimental absorbance-time data pairs were fitted to the exponential function:

$$(A_\infty - A_t) = (A_\infty - A_0) \exp(-k_{\text{obs}} t)$$

$$\text{or} \quad \ln \left(\frac{A_\infty - A_t}{A_\infty - A_0} \right) = -k_{\text{obs}} t \quad (4)$$

where A_t is the absorbance of the reaction mixture which is mainly due to MnO_4^{2-} at a given time (t) through the reaction, A_0 is its initial absorbance ($t = 0$) and A_∞ is the absorbance of the mixture at the end of the reaction, that is when the absorbance no longer changes with time ($t = \infty$).

Experimental results showed that a plot of $\ln [(A_\infty - A_t)/(A_\infty - A_0)]$ vs. time gives a straight line. Its slope represents the rate of appearance of MnO_4^{2-} , which equals the rate of disappearance of MnO_4^- (as shown in the suggested mechanism below). The value of k_{obs} (s^{-1}) was obtained from the slope, according to eqn. 4. Using eqn. 3, a plot of $\ln k_{\text{obs}}$ vs. $\ln [\text{ATN}]^a$ is a straight line that gives the reaction rate constant, k , in units of $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (intercept) and the order of the reaction (a) with respect to $[\text{ATN}]$ (slope). At specific concentrations of substrate and oxidant several trials were carried out for each measurement and the average value of the observed rate is reported. Two observed rates were found ($k_{\text{obs}1}$ and $k_{\text{obs}2}$) and hence, two different reaction rate constants are obtained. Experimental errors in value of rate constant are estimated to be $\pm 10 \%$.

The kinetics results for the oxidation of atropine by KMnO_4 are shown in Table-1 and sample plots are shown in Figs. 3-6.

TABLE-1
CONCENTRATION EFFECT ON RATE OF OXIDATION OF ATROPINE BY KMnO_4 IN AQUEOUS BASIC SOLUTIONS, $[\text{KOH}] = 0.10 \text{ M}$

[ATN] = $1.0 \times 10^{-2} \text{ M}$				[MnO_4^-] = $1.0 \times 10^{-3} \text{ M}$			
Run	[KMnO_4] M	$k_{\text{obs1}} \times 10^3$	$k_{\text{obs2}} \times 10^3$	Run	[ATN] M	$k_{\text{obs1}} \times 10^3$	$k_{\text{obs2}} \times 10^3$
1	2.00×10^{-3}	2.26	5.26	5	1.75×10^{-2}	2.80	6.51
2	1.75×10^{-3}	2.13	5.64	6	1.50×10^{-2}	2.66	6.30
3	1.50×10^{-3}	2.18	5.27	7	1.00×10^{-2}	2.25	5.40
4	1.00×10^{-3}	2.25	5.40	8	0.50×10^{-2}	1.91	3.79

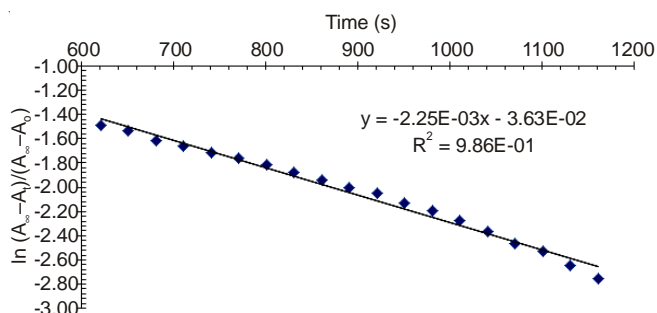


Fig. 3. Sample plot for rate of step 2 of $\ln [(A_\infty - A_t)/(A_\infty - A_0)]$ vs. time; $[\text{ATN}] = 1.0 \times 10^{-2} \text{ M}$, $[\text{KMnO}_4] = 1.0 \times 10^{-3} \text{ M}$, $[\text{KOH}] = 0.10 \text{ M}$

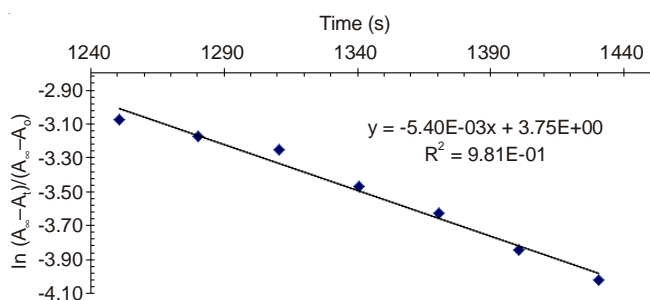


Fig. 4. Sample plot for rate of step 5 of $\ln [(A_\infty - A_t)/(A_\infty - A_0)]$ vs. time; $[\text{ATN}] = 1.0 \times 10^{-2} \text{ M}$, $[\text{KMnO}_4] = 1.0 \times 10^{-3} \text{ M}$, $[\text{KOH}] = 0.10 \text{ M}$

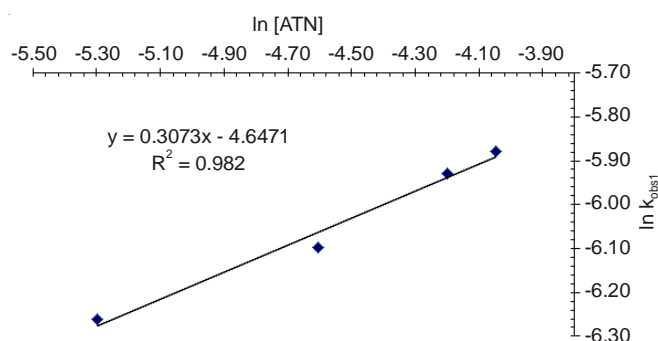


Fig. 5. Sample plot for rate of step 2 of $\ln [\text{ATN}]$ vs. $\ln k_{\text{obs1}}$; $[\text{KMnO}_4] = 1.0 \times 10^{-3} \text{ M}$, $[\text{KOH}] = 0.10 \text{ M}$

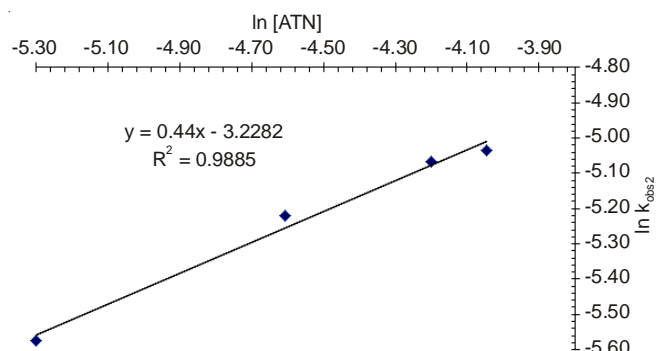
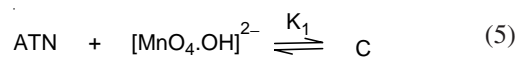


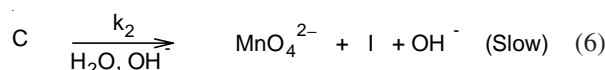
Fig. 6. Sample plot for rate of step 4 of $\ln [\text{ATN}]$ vs. $\ln k_{\text{obs2}}$; $[\text{KMnO}_4] = 1.0 \times 10^{-3} \text{ M}$, $[\text{KOH}] = 0.10 \text{ M}$

Based on the obtained kinetics results, we propose the following mechanism for the oxidation process of atropine.

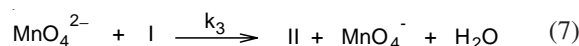
Step 1



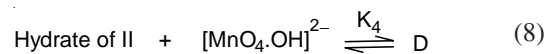
Step 2



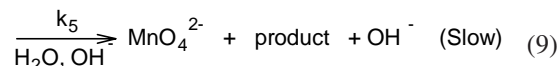
Step 3



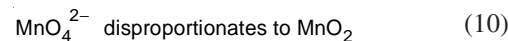
Step 4



Step 5



Step 6



where C and D are complexes, I and II are intermediates.

In a strongly basic solution, MnO_4^- will be in the form of $[\text{MnO}_4\text{OH}]^{2-}$. Experimentally, the reaction rate was followed by monitoring the change in absorbance of the reaction mixture with time at $\lambda = 440 \text{ nm}$. At this wavelength, the absorbance (A_t) is mainly due to the formation of MnO_4^{2-} (Fig. 2) and it is increasing with time. Due to regeneration of MnO_4^- from MnO_4^{2-} (eqn. 7), then the rate of formation of MnO_4^{2-} is approximately equal to the rate of disappearance of MnO_4^- .

Oxidation of primary alcohols under strongly alkaline KMnO_4 is known to occur in two stages²³. For the first stage, an aldehyde intermediate is well-established. Further oxidation of the aldehyde to the final product (carboxylic acid) proceeds at a faster rate compared to the first stage.

Fig. 7 depicts the absorbance change $\ln \left(\frac{A_\infty - A_t}{A_\infty - A_0} \right)$ over

the whole reaction time. Clearly the reaction is governed by two distinctive rates. The reason for two stages is based on the fact that intermediates are reaching their optimum concentration or due to the occurrence of consecutive reactions²⁴. At the first stage (steps 1-3) of the reaction, the absorbance increased rapidly with time that indicating that oxidation of atropine to intermediate I which is relatively slow (compared with stage 2 (steps 4 and 5)). The rate limiting step of this stage is represented by step 2 (eqn. 6). However; at certain time when an optimum concentration of intermediate II (then the hydrate form of the aldehyde)²⁵ is reached, the reaction will be controlled by step 5 (eqn. 9) that is faster than the first limiting step 3. Finally oxidation of intermediate II proceeds cleanly to produce the final products.

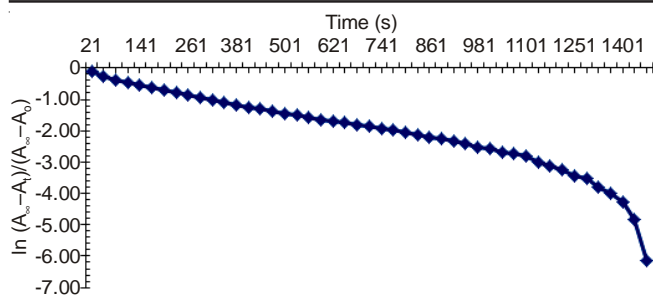


Fig. 7. Plot of $\ln(\text{absorbance})$ vs. time for the reaction mixture at $\lambda_{\text{max}} = 440$ nm; $[\text{KMnO}_4] = 1.00 \times 10^{-3}$ M, $[\text{ATN}] = 1.00 \times 10^{-2}$ M, $[\text{OH}^-] = 0.10$ M

The change in absorbance with time represents the rate of the reaction according to eqn. 2. From a kinetic point of view, steps 2 and step 5 will be the rate determining steps and steps 1, 3, 4, 6 are fast. Experimentally, two rates were observed. The first reaction rate (rate 1) is due to step 2, consequently, eqn. 1 above can be rewritten as:

Rate 1 = $k_2[\text{C}]$ and from eqn. (5), $[\text{C}] = K_1[\text{ATN}][\text{MnO}_4^-]$ and, $[[\text{MnO}_4 \cdot \text{OH}]^{2-}] = [\text{MnO}_4^-]$, then

$$\text{Rate 1} = k_2 K_1 [\text{ATN}][\text{MnO}_4^-]$$

Here, $k_2 K_1$ is a constant quantity which represents the first rate of the reaction and will be represented as k_{rxn1} . Then,

$$\text{Rate 1} = k_{\text{rxn1}} [\text{ATN}]^a [\text{MnO}_4^-]^b \quad (11)$$

The second reaction rate (rate 2) is due to step 5, given by:

$$\text{Rate 2} = k_5 [\text{D}]$$

From eqn. 8, $[\text{D}] = K_4[\text{Hydrate of II}][\text{MnO}_4^{2-}]$ and, $[\text{Hydrate of II}] = [\text{II}] = [\text{ATN}_{\text{reacted}}]$, then

$$\text{Rate 2} = k_5 K_4 [\text{Hydrate of II}][\text{MnO}_4^{2-}]$$

The concentration of MnO_4^{2-} produced equals to the concentration of reacted MnO_4^- . The constant quantity $k_5 K_4$ represent the second rate of the reaction and will be called k_{rxn2} . Then:

$$\text{Rate 2} = k_{\text{rxn2}} [\text{ATN}_{\text{reacted}}]^a [\text{MnO}_4^-]^b \quad (12)$$

A strong reason why a λ_{max} at 440 nm, which is specific for MnO_4^{2-} , was selected is due to the formation of MnO_4^{2-} in both of the slow steps 2 and 5. The disappearance of the distinct permanganate absorbance band located in the range of wavelengths 490-590 nm and the formation of bands with maxima at 347, 439 and 606 nm (Fig. 2) are characteristic of manganate MnO_4^{2-} , supports this observation. Disproportionation of manganate to form permanganate and manganese dioxide is then follows²⁵. Possible structures of the intermediates and complexes involved are shown in Fig. 8. It is worth mentioning that the proposed structures of these intermediates are not conclusive but highly possible²⁶. The aldehyde-intermediate(II) is logical since it is a common intermediate for similar oxidations (e.g., $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation)²⁷. Wiberg and Stewart²⁵ demonstrated the free radical mechanism of oxidation of aldehydes by alkaline KMnO_4 solution. Formation of permanganate ester of the hydrate of the aldehyde was also implicated. The regenerated permanganate present in the form $(\text{MnO}_4 \cdot \text{OH})^{2-}$ will react preferentially with intermediate II rather than the excess atropine, since it is known that aldehydes are more reactive compared to primary alcohols toward the permanganate oxidizing reagent. This step involves a second single electron transfer.

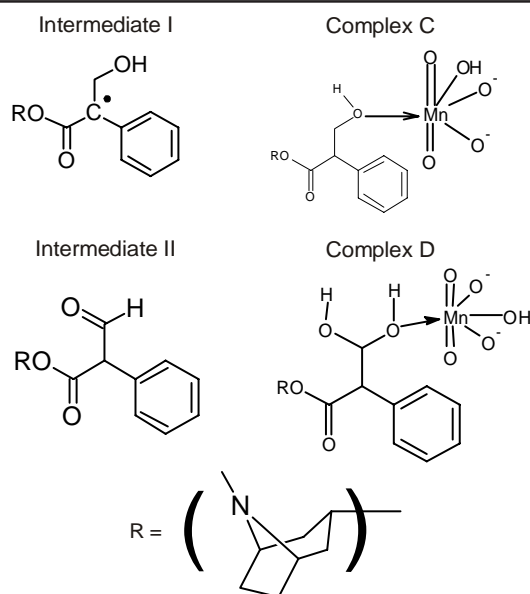


Fig. 8. Possible structures of intermediates and complexes involved in the proposed mechanism

The above proposed mechanism is supported by the observation of initial colour change of permanganate from violet to green (manganate). The radical mechanism was invoked due to the precipitation observed when mercuric chloride was added to the system²⁸. When HgCl_2 was added after the appearance of the green colour, the colour persists. The reaction was quenched at this stage.

Since the observed overall rate was obtained to be first order with respect to permanganate, eqns. 11 and 12 above will have the following expression

$$\text{Rate} = k_{\text{obs}} [\text{MnO}_4^-] \quad (13)$$

And since $[\text{ATN}] \gg [\text{KMnO}_4]$, the observed rate of the reaction, k_{obs} , is given by:

$$\text{For step 2: } k_{\text{obs1}} = k_{\text{rxn1}} [\text{ATN}]^a$$

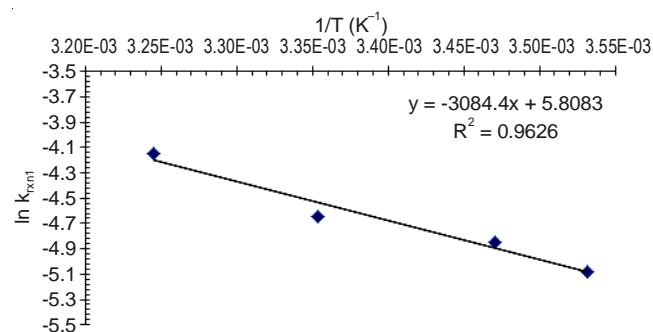
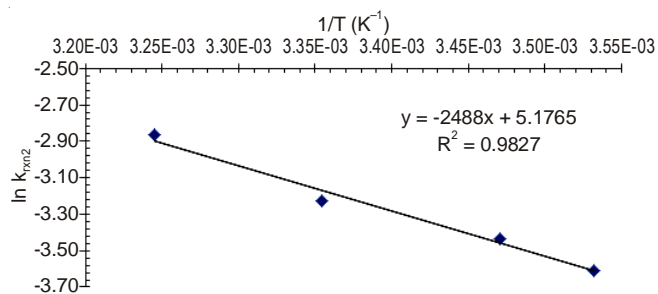
$$\text{For step 5: } k_{\text{obs2}} = k_{\text{rxn2}} [\text{ATN}]^a \quad (14)$$

The rates constant k_{rxn1} and k_{rxn2} were obtained from plots of $\ln k_{\text{obs1}}$ vs. $\ln [\text{ATN}]$ and $\ln k_{\text{obs2}}$ vs. $\ln [\text{ATN}]$, respectively.

Effect of temperature on rate constant was studied. Results are shown in Table-2. Each value in the table is the average of several runs. Experimental errors in the rate constant are estimated to be $\pm 10\%$. As expected, results show that the rate constant (k_{rxn2}) for step 5 is greater than that for step 2 (k_{rxn1}). The activation energy (E_a) for both steps 2 and 5, were calculated using Arrhenius equation. From plots of $\ln k$ vs. $(1/T)$ for both steps (Figs. 9 and 10), E_a 's of 25.64 and 20.69 KJ for steps 2 and 5, respectively. Apparently; the thermodynamics is in

TABLE-2
REACTION RATES FOR OXIDATION OF ATROPINE BY KMnO_4 IN AQUEOUS BASIC SOLUTIONS AT VARIOUS TEMPERATURES; $[\text{ATN}] = 1.0 \times 10^{-2}$ M, $[\text{MnO}_4^-] = 1.0 \times 10^{-3}$ M, $[\text{KOH}] = 0.10$ M

Temp. (°C)	k_{rxn1} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	k_{rxn2} ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
10.0	6.21×10^{-3}	2.72×10^{-2}
15.0	7.85×10^{-3}	3.22×10^{-2}
25.0	9.59×10^{-3}	3.96×10^{-2}
35.0	15.90×10^{-3}	5.70×10^{-2}

Fig. 9. Plot of $\ln k_{rxn1}$ vs. $(1/T)$ for step 2Fig. 10. Plot of $\ln k_{rxn2}$ vs. $(1/T)$ for step 5

agreement and proportional to the related rate constants determined for these steps.

Conclusion

Reaction and kinetics of the oxidation of the biologically important atropine by alkaline KMnO_4 was studied. Experimental observations show that the reaction proceeds *via* two stages to give the final products: tropine and phenylmalonic acid. Two rate determining steps with different rates were proposed, which were in agreement with obtained kinetic result. A proposed mechanism for the process is presented. The mechanism suggests the formation of two intermediates in two stages of the reaction with different rates and activation energies.

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