# KINETICS AND MECHANISM OF OXIDATION OF CINNAMYL ALCOHOL BY THALLIUM(III) IN ACID PERCHLORATE MEDIUM

[1]ANITA MEENA, [2]RIYA SAILANI, [3]PRIYAMVADA SHARMA & [4]C.L. KHANDELWAL
[1] ASST. PROFESSOR, [2] ASST. PROFESSOR, [3] ASST. PROFESSOR & [4] ASSOCIATE PROFESSOR

[1] Department of Chemistry, JNVU, Jodhpur, Rajasthan, India

ABSTRACT

The kinetics and mechanism of oxidation of cinnamyl alcohol by thallic perchlorate has been studied in aqueous acid medium. The Stoichiometry of the reaction corresponds to the reaction as represented by the equation.

$$Tl(III)+C_6H_5-CH=CH-CH_2OH \rightarrow Tl(I)+C_6H_5-CH=CH-CHO+2H^+$$
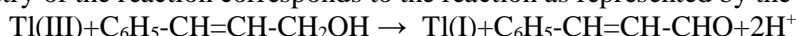
The reaction has been observed to be bimolecular viz. first order with respect to oxidant and substrate respectively. The oxidation product of alcohol has been established to be aldehyde by preparing its 2,4-dinitrophenylhydrozone.Tl(I) was qualitatively tested by precipitating thallus iodide. A plausible reaction mechanism accounting for retarding effect of hydrogen ion concentration has been suggested and the rate law derived from such a mechanism accounts for experimental observation.

Key words: Kinetics, Mechanism, Oxidation, Cinnamyl Alcohol, Thallium.

INTRODUCTION:

A large number of research papers on oxidation of organic compounds with varying functional groups of different reactivities by thallium(III) in aqueous acid perchlorate medium have been reported[1-21]. The unique reactivity and selectivity of thallium(III) have been indicated in such reactions more particularly where the mixture of oxidant products of the substrate have been found. Apart from this the synthetic potential of thallium(III) has also been explored in preparation of certain organo-thallium(III) derivatives. Such derivatives on solvolysis of Carbon-Thallium bond are understood to yield oxidation products[22].

Since thallium(II) is reported to be an intermediate in oxidation reaction of thallium(III), the role of thallium(II) in majority of reactions has not yet been fully established. However, there are certain reactions where thallium(II) has been synthesized and employed in reactions to understand its reactivity.

The main aim to undertake the above titled study was to understand the role of thallium(III) as an oxidant towards unsaturated alcohols. Moreover the attack of oxidant on primary alcoholic group or C=C in the alcohol is yet to be established. Secondly we were also interested to know whether any intermediate complex is formed between oxidant and substrate. If so, what type of role it plays in the reaction mechanism is an important aspect to probe? Thirdly what type of pattern of reactivity of thallium(III) towards such alcohols is similar as is obtaining in case of saturated alcohols.

EXPERIMENTAL

Materials and Method

Thallium(III) perchlorate solution was prepared by dissolving thallic oxide(Fluka AR) in 70% perchloric acid (E.Merck) at 60-70° C. Thallic oxide was added in different small lots with constant stirring till the resulting solution turned out to be colourless, heating was stopped and the solution was kept at ambient temperature overnight . This stock solution was further diluted by addition of water with continuous shaking and then left for 24 hours for settling of the undissolved material, if any. This solution was then decanted and was used as stock solution of thallium(III) perchlorate. This was quite stable and showed no change in its titre values for more than a year, provided concentration of perchloric acid was kept at $\geq$ 2.0 mol dm^{-3}. The solution was standardized iodomatrically. The acid contents of the solution were determined by titrating the known aliquot of the solution against the standard solution of sodium hydroxide in the presence of KBr. The addition of KBr was necessitated to check hydrolysis of thallium(III) towards the end of the titration owing to an increase of pH of the titrating mixture. The addition of KBr formed strong bromo-thallium(III) complexes checking hydrolysis and detection of the end-point without any interference.

Cinnamyl alcohol (Alfa Aesar) is partially miscible in water and in aqueous acids. Therefore, the solutions of cinnamyl alcohol were prepared by dissolving an appropriate amount of the alcohol in doubly distilled water.

Kinetic Procedure

The experiments were carried out taking all reagents in Erlenmeyer flasks which were painted black in the outside and were suspended in a water bath thermostated at ±0.1°C.Thallium(III) solution was taken in another flask and also

temperature equilibrated in the same thermostated water bath. A requisite amount of thallium(III) solution was taken out and then discharged into the reaction mixture. The kinetics of the reaction was monitored iodometrically[23,24] withdrawing an aliquot (5 cm^3) at different time intervals. The time of initiation of the reaction was recorded when half of the thallium(III) contents from the pipette were released into the reaction mixture. A 10% solution of KI was prepared in which aliquot of the reaction mixture was discharged. The liberated iodine was titrated against thiosulphate solution to the golden yellow colour as end-point. However, the titration should be carried out with vigorous shaking. It is essentially required as the liberated iodine adsorbed by thallous iodide is released during titration and it not been return it could have been with some error.

Initial rates (k_i mol dm^{-3} sec^{-1}) were computed by employing glass mirror method[25]. Second order rate constants were calculated for comparable concentrations of the reactants. The second order rate constants obtained from second order plots were in agreement with the second order rate constants evaluated from initial rates confirming nature of the reaction to be overall second order. Rates in triplicate were reproducible. Doubly distill water was employed throughout the study. The second distillation was from alkaline permanganate solution in an all glass apparatus.

Stoichiometry and Product Analysis

The stoichiometry of the reaction was calculated by undertaking thallium(III) in excess over alcohol after ensuring the reaction. Excess thallium(III) was estimated iodometrically. The results indicate that a mole of thallium(III) required a mole of cinnamyl alcohol. However this was further confirm by undertaking kinetics of reactions under this stoichiometric conditions and second order plots were made (fig 1). Second order rate constants calculated from these plots were in agreement to those as mention in Table 1. Further confirmation of such stoichiometry was established by product analysis of the oxidation product of substrate. The reduction product of Tl(III) to be Tl(I) was qualitatively established by precipitating thallium(I) as thallous iodide- an orange yellow coloured compound. The oxidation product of alcohol was established by adding 2,4-Dinitrophenylhydrazine(2,4-DNP) into HCl medium. HCl was added in the reaction mixture prior to addition of 2,4-DNP so that precipitated thallous chloride was removed through filtration. The reaction mixture after addition of 2,4-DNP was left overnight at refrigerated temperature (~5°C). The golden yellow precipitate of 2,4-Dinitrophenylhydrazone was found settled at the bottom of the flask. The solution was decanted off and the precipitate was collected and vacuum dried for spectral analysis such as IR and NMR.
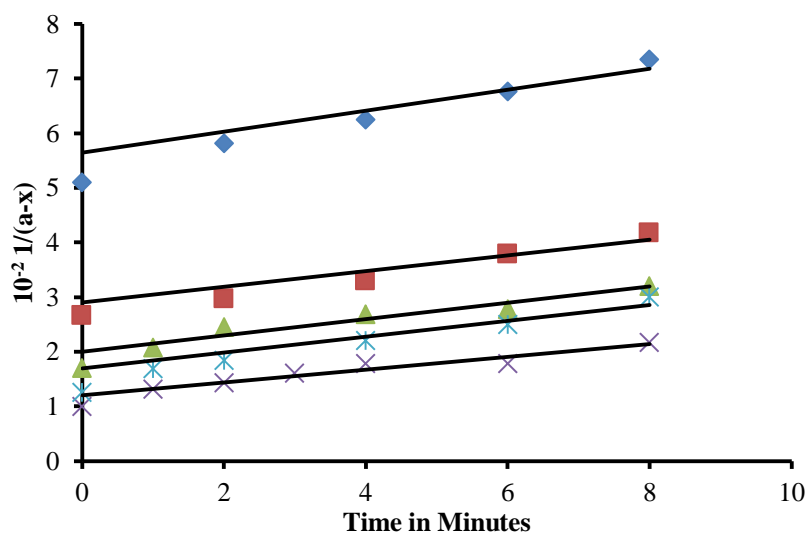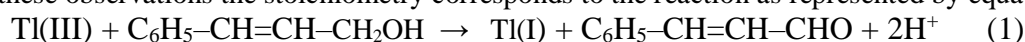

Fig. 1 : Stoichiometric plots

[HClO$_4$] = 5.0 mol dm^{-3}; [NaClO$_4$] = 0.5 mol dm^{-3}

[Tl (III)] : [CAL] ◆ 2.0 × 10^{-3}: 2.0 × 10^{-3} ;

     ■ 4.0 × 10^{-3}: 4.0 × 10^{-3}; ▲ 6.0×10^{-3} : 6.0×10^{-3} ;

    ✳ 8.0 × 10^{-3}: 8.0 × 10^{-3}; × 10.0 × 10^{-3} : 10.0 × 10^{-3} mol dm^{-3} and 35°C

Thus based on these observations the stoichiometry corresponds to the reaction as represented by equation (1)

$$Tl(III) + C_6H_5-CH=CH-CH_2OH \rightarrow Tl(I) + C_6H_5-CH=CH-CHO + 2H^+ \qquad (1)$$

RESULTS

Thallium(III) Dependence:-

The concentration of Thallium (III) was varied keeping fixed concentration of other reaction parameters and I = 1.0 mol dm^{-3} (where I is ionic strength adjusted by employing sodium perchlorate) at 35°C. Initial rates k_i, mol dm^{-3} sec^{-1} were calculated and a plot of k_i v/s Tl(III) was made that yielded a straight line passing through the origin confirming first order dependence with respect to thallium(III).

Also second order plots were made for comparable concentration of the reactants. The second order rate constants evaluated from these plots were in agreement to the rate constants calculated by second order plots.

Cinnamyl Alcohol dependence

The concentration of cinnamyl alcohol was varied at constant concentration of other reaction parameters and I = 1.0 mol dm^{-3} at 35°C. A plot of k_i (mol dm^{-3} sec^{-1}) v/s concentration of cinnamyl alcohol were made and a straight line passing through the origin and also second order plots for comparable concentration of the reactants were made.

Ionic strength dependence

The effect of ionic strength was made by undertaking reactions. A plot of initial rate v/s μ was made that yielded a straight line passing through origin. The rate increases with increasing ionic strength.
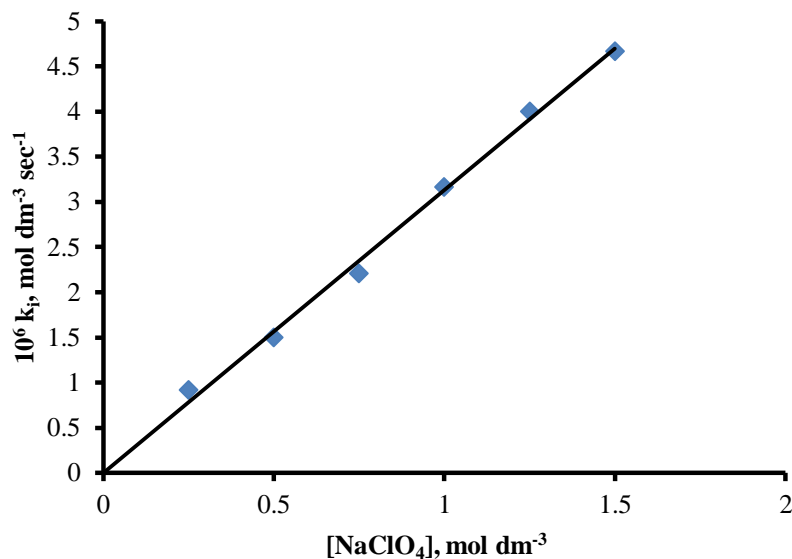

Fig. 2: Variation of sodium perchlorate.

[Tl(III)] = 1.0 × 10^{-3} mol dm^{-3}; [CAL] = 5.0×10^{-3} mol dm^{-3};
[HClO$_4$] = 0.5×10^{-3} mol dm^{-3} and 35°C

Effect of hydrogen ion

The effect of hydrogen ion on the rate of reaction was studied by employing perchloric acid at fixed ionic strength to be 2.0 mol dm^{-3} and also fixed concentration of other reaction parameters. The rate decreases with increasing hydrogen ion concentration.
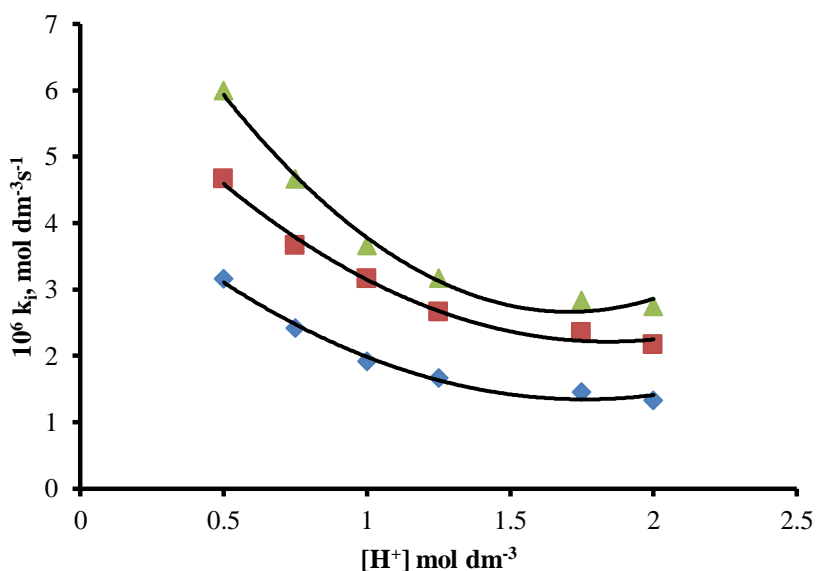
Fig. 3: Variation of hydrogen ion.
[Tl(III)] = 1.0×10^{-3} mol dm^{-3}; [CAL] = 5.0×10^{-3} mol dm^{-3};

I = 2.0 mol dm^{-3}; ◆ 30°C; ■ 35°C ▲ 40°C

Effect of temperature

Effect of temperature was studied at three temperature viz. 30, 35, 40 °C respectively keeping fixed concentration of other reaction ingredients. The energy and entropy of activation was calculated by employing erying plot. Energy of activation 47.89 ± 0.7 kJ mol^{-1} and Entropy are -90.62 ± 2.24 JK^{-1}mol^{-1}.
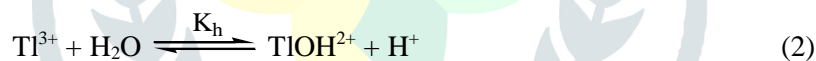
Effect of free radicals

The test of free radicals was made by undertaking the reaction at fixed concentration of Thallium(III), Cinnamyl alcohol and HClO$_4$ by adding acrylic acid or acrylonitrile, no white sediment even after two half lives of the reaction was observed. This negatives the participation of free radicals, it appears that a free radical "if formed" that remains in the solvent cage. As soon as it is formed, it immediately reacts and thus does not find time to diffuse out of the solvent cage to react the monomer for its polymerisation.

DISCUSSION

Thallium(III) despite being significantly stable reportedly[26] undergoes hydrolysis in dilute acid solutions as represented by equation

$$Tl^{3+} + H_2O \xrightleftharpoons{K_h} TlOH^{2+} + H^+ \tag{2}$$

The hydrolytic constant (K_h) was variously reported viz. 0.086 at 25°C which was estimated to be 0.088 at 30°C employing enthalpy change of hydrolysis (69.4 kJ mol^{-1}). Since rate is retarded by hydrogen ion concentration, the hydrolyzed species TlOH^{2+} rather Tl^{3+}$_{(aq)}$ appears to be the reactive form. TlOH^{2+} has also been reported[27-31] to be the reactive species in other reactions and hence it is not unique observation in reactions of thallium(III). Cinnamyl alcohol is in its molecular form as no protonation of such an alcohol is reported. Thus a bimolecular interaction of TlOH^{2+} and cinnamyl alcohol appears to be the rate controlling step (heretofore cinnamyl alcohol is written as CAL). However, prior to rate determining step an adduct formation between TlOH^{2+} and CAL appears to be more logical as it will provide a more facile pathway energetically in preference to bimolecular interaction. Therefore, in view of the observed stoichiometry overall second order viz. first order with respect to the oxidant and substrate respectively and inverse hydrogen ion dependence of the rate, the following reaction mechanism can be envisaged to account for these experimental observations.

$$Tl^{3+} + H_2O \xrightleftharpoons{K_h} TlOH^{2+} + H^+ \tag{2}$$

$$TlOH^{2+} + CAL \xrightleftharpoons{K} [Adduct]^{\#} \tag{3}$$

$$[Adduct]^{\#} \xrightarrow{k'} Products \tag{4}$$

Such a mechanism leads to the rate law (5)

$$-\frac{d[Tl(III)]}{dt} = \frac{k' K K_h [Tl(III)][CAL]}{[H^+] + K_h + K K_h [CAL]} \tag{5}$$

Here two important experimental aspects are to be taken into account for analysis of rate parameters from rate law (5). First we do not have any experimental (both kinetic and spectral) evidence to support the formation of intermediate complex. Also order with respect to the substrate is one. Second the equilibrium constant K is insignificant. If an inequality ($[H^+]+K_h$) $\gg$ $K K_h$ [CAL] is valid in view of first order dependence with respect to CAL and insignificant equilibrium step (3), the rate law (5) is reduced to (6)

$$-\frac{d[Tl(III)]}{dt} = \frac{k K_h [Tl(III)][CAL]}{[H^+] + K_h} \tag{6}$$

where k = k'K, [Tl(III)] and [CAL] are the gross analytical concentrations of thallium(III) and Cinnamyl alcohol respectively. Such a rate law (6) is adequately in agreement of experimental observations.

Rate law (6) is further reduced to eqn (7),

$$-\frac{(-d[Tl(III)]/dt)}{[Tl(III)](CAL)} = k_{obs} = \frac{k K_h}{[H^+] + K_h} \tag{7}$$

The double reciprocal of eqn (7) yields eqn (8)

$$1/k_{obs} = \frac{[H^+]}{k K_h} + \frac{1}{k} \tag{8}$$

A plot of $1/k_{obs}$ versus $[H^+]$ was made from equation (8) that yielded a straight line with non-zero intercept (Fig. 4) 'k' was calculated from the intercept to be 0.769, 1.333 and 2.0 dm^3 mol^{-1} s^{-1} at I = 2.0 mol dm^{-3} and also 30, 35 and 40°C respectively. Similarly the ratio of intercept and slope yielded K_h to be 1.06, 0.935 and 0.68 at I = 2.0 mol dm^{-3} and at 30, 35 and 40°C respectively.
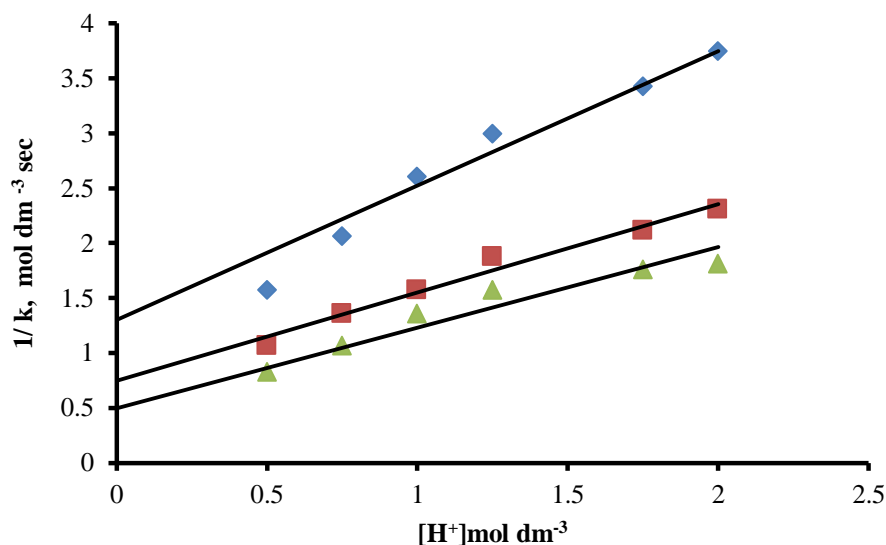
Fig. 4: A plot of 1/k versus [H⁺]
$[Tl(III)]$ = 1.0×10^{-3} mol dm^{-3}; $[CAL] = 1.0 \times 10^{-3}$ mol dm^{-3};
$[HClO_4] = 0.5$ mol dm^{-3} ; $[NaClO_4] = 1.5$ mol dm^{-3} and 35°C

The values of K_h are in agreement to the values reported earlier if effect of ionic strength is taken into account.
The water-exchange rate constant to be $\sim 3 \times 10^8$ dm^3 mol^{-1} s^{-1} is reported in case of aqua thallium(III) in view of thallium(III) is known as substitution labile. Since the rate of complex formation is independent of the nature of the incoming ligand, the dissociation of aqua ligand should be the rate determining step in substitution reactions of thallium(III). However, the rate constant observed in this reaction is much lower than expected from the rates of substitution in thallium(III), such an observation certainly negates the complex formation between oxidant and substrate to be the rate determining step. Therefore, the reaction in all probability appears to be redox controlled.
So far the probable mode of electron transfer from the substrate to the oxidant is concerned; the most favorable account of reaction events via redox rupturing of intermediate adduct is energetically more facile rather than a bimolecular encounter of reactants. Such events of the reaction can be envisaged as in scheme-I.
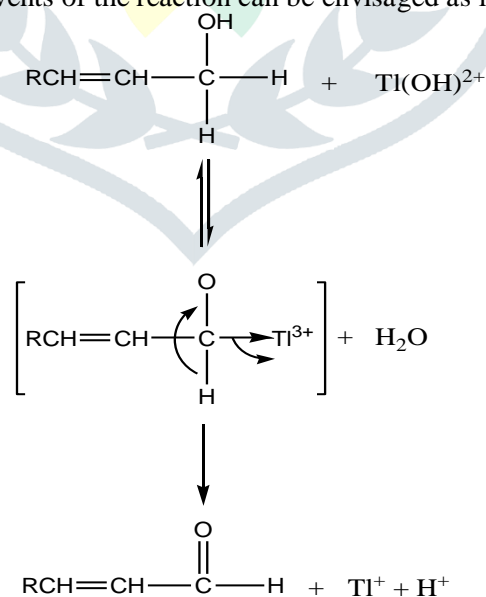
Where R = C_6H_5
Scheme-I

Such a scheme-I suggests a complex (adduct) between (+)ve ion (TlOH²⁺) and a dipolar alcohol (CAL) which in turn oxidatively ruptures into products by the elimination of hydride ion from the α-carbon of alcohol. The scheme being in agreement to the observed effect of ionic strength on the rate. Thus the proposed scheme-I accounts for the course of the reaction events.
The order of reactivity of unsaturated alcohols towards thallic ion has also been observed in the following sequence.

Cinnamyl alcohol > Crotyl alcohol > Allyl alcohol

Such a greater reactivity of Cinnamyl alcohol than that of crotyl alcohol or allyl alcohol can be assigned to resonance stabilization and greater (+)ve character of the transition state. Moreover, unsaturated acids such as acrylic acid and cinnamic acid do not undergo oxidation under the experimental conditions ascribing to the fact that >C< bond is not attacked by thallium(III) and remains intact.

Moreover, oxidation of unsaturated cinnamyl alcohol is much faster than that of its saturated analogue by thallium(III). Such a reactivity difference can be attributed to highly reactive mesomeric intermediate such as ($^+CH_2$-CH=CH-OH), (CH_2=C–$^+$CH-OH) which are considered to be highly reactive. Similar trend is also reported by Jones and Waters[32], Rao et al.[33] in the oxidation of allyl and crotyl alcohol.

The energy of activation being very close to a bimolecular reaction also supports weak complex between oxidant and substrate ascribing the reaction to be enthalpy controlled.

The reaction did not show formation of any free radical. The standard oxidation potential of the redox complex Tl^{II}/Tl^{I} is much larger than that of Tl^{III}/Tl^{I} redox couple ascribing Tl^{II} to be stronger oxidizing agent than Tl^{III}. There is every possibility of formation of Tl^{II} in initial interaction and remains in the solvent cage and reacts with the substrate before diffusing out of the cage. This eliminates the chances of formation of free radicals in the reaction.

Table-3.8

Initial rates (k_i, mol dm^{-3} sec^{-1}) and second order rate constants in the reaction of Tl(III) and cinnamyl alcohol.
[HClO$_4$] = 0.5 mol dm^{-3} [NaClO$_4$] =0.5 mol dm^{-3} ,temp. = 35°C

10^3[Tl(III)] mol dm^{-3}	10^3[CAL] mol dm^{-3}	10^6 (k_i) mol dm^{-3} sec^{-1}	(k) dm^{3}mol^{-1}sec^{-1}
1.0	10.0	1.66	0.17(0.19)
1.5	10.0	2.5	0.17(0.18)
2.0	10.0	3.5	0.18(0.18)
2.5	10.0	4.17	0.17(0.19)
3.0	10.0	5.0	0.17(0.19)
3.5	10.0	6.13	0.18(0.18)
4.0	10.0	7.08	0.18(0.19)
4.5	10.0	7.88	0.18(0.19)
5.0	10.0	8.75	0.18(0.19)
1.0	5.0	0.83	0.17(0.19)
1.5	5.0	1.49	0.19(0.19)
2.0	5.0	1.66	0.17(0.19)
2.5	5.0	2.08	0.17(0.19)
3.0	5.0	2.66	0.18(0.19)
3.5	5.0	3.21	0.18(0.19)
4.0	5.0	3.67	0.18(0.19)
4.5	5.0	3.96	0.18(0.19)
5.0	5.0	4.38	0.18
1.0	1.0	0.17	0.17
1.0	2.0	0.33	0.17
1.0	3.0	0.5	0.17
1.30	4.0	0.66	0.17
1.0	5.0	0.83	0.17(0.19)
1.0	7.0	1.17	0.17(0.19)
1.0	8.0	1.42	0.18(0.19)
1.0	10.0	1.66	0.17(0.19)
1.0	15.0	2.5	0.17(0.19)
1.0	20.0	3.17	0.16(0.18)

2.0	2.0		0.23*
4.0	4.0		0.23*
6.0	6.0		0.23*
8.0	8.0		0.23*
10.0	10.0		0.23*

Second order rate constants calculated from second order plots are in parenthesis
*Second order rate constants calculated from Stoichiometric Concentrations

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