

## Kinetic study on oxidation of 2-Aryl-*trans*-decahydroquinoline-4-ones by LTA

K.Udaya Lakshmi<sup>1</sup>, N.Sharmila<sup>1</sup>, B.Nageswara Rao<sup>1</sup>, G.V.Ramana<sup>2</sup>, B.Hari Babu<sup>1\*</sup>,  
P.V.V.Satyanarayana<sup>1</sup>

<sup>1</sup>Department of Chemistry, Acharya Nagarjuna University, Nagarjunanagar, Guntur-522510, Andhra Pradesh, (INDIA)

<sup>2</sup>Department of Chemistry, Andhra Loyola College, Vijayawada, (INDIA)

E-mail : dr.b.haribabu@gmail.com

### ABSTRACT

A kinetic study was carried out on the oxidation of some substituted 2-aryl-*trans*-decahydroquinolin-4-ones in the presence of glacial acetic acid by using LTA as oxidizing agent. The order of the reaction was found to be overall second order, first order each with respect to ketone and oxidant LTA. The introduction of electron releasing groups on *para* position of the aryl group at position 2 increased the rate of oxidation and more over the substitution of the methyl group at position 3 in the decalin ring decreased the rate of oxidation of the ketones. A change in the rate of oxidation of the ketone was found to increase with increase in temperature.

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### KEYWORDS

Kinetics;  
LTA;  
Oxidation;  
2-aryl-*trans*-  
decahydroquinolin-4-ones.

### INTRODUCTION

The Kinetic studies on the oxidation of different aliphatic<sup>[1-4]</sup>, alicyclic<sup>[5-8]</sup>, aromatic<sup>[9-12]</sup> ketones and a series of 2,6-diaryl-4-piperidones<sup>[13,14]</sup> have been studied extensively by various workers and suitable mechanisms have been proposed. However, the kinetic studies on oxidation of 2-aryl-*trans*-decahydroquinolin-4-ones have received less attention. Recently satyanarayana<sup>[15,16]</sup> studied the kinetics of oxidation of the present ketone system in aqueous acetic acid using thallium (III) and cerium (IV) as oxidants. Hence, the author has taken up the kinetic studies on oxidation of 2-aryl-*trans*-decahydroquinolin-4-ones with a view to extend the study leads to substituent effects on the rate of oxidations, to identify the possible product (s) formed in the oxidation and to give a possible mechanism of the oxidation process. For this purpose the author has pre-

pared total eight ketones (Figure 1) by the method already reported by Balaih and Natarajan<sup>[17]</sup>.

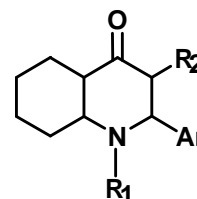


Figure 1: 2-aryl-*trans*-decahydroquinolin-4-ones

S.No.	Ar	R <sub>1</sub>	R <sub>2</sub>
1.	C <sub>6</sub> H <sub>5</sub>	H	H
2.	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	H	H
3.	<i>p</i> -OMe-C <sub>6</sub> H <sub>4</sub>	H	H
4.	C <sub>6</sub> H <sub>5</sub>	H	Me
5.	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	H	Me
6.	<i>p</i> -OMe-C <sub>6</sub> H <sub>4</sub>	H	Me
7.	C <sub>6</sub> H <sub>5</sub>	Me	Me
8.	<i>o</i> -Cl-C <sub>6</sub> H <sub>5</sub>	H	H

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### EXPERIMENTAL

#### Purification of materials

The required ketones were purified by recrystallisation from suitable solvents to constant melting points. All the samples were dried in vacuum before use.

#### Acetic acid

Acetic acid glacial (Excelar), supplied by "Qualigens Fine Chemicals", a division of Gloxo India Limited, was refluxed with chromium trioxide and acetic anhydride for six hours and fractionally distilled. The fraction at 117-118°C was used.

#### Other reagents

Sulphuric acid (A.R), potassium iodide (A.R), potassium dichromate (A.R) were used. Doubly distilled water was used for all purposes.

#### Kinetic procedure

Iodometric<sup>[18]</sup> procedure was followed for all kinetic runs. Measurements were made at 30, 35, 40 and 45 °C. The temperature was controlled by using thermostat of accuracy  $\pm 0.1^\circ\text{C}$ . Measurements were made with volumetric glassware calibrated in the usual way. The required amount of LTA solution was prepared by dissolving the necessary amount of leadtetraacetate in the solvent medium. The medium used was 98% acetic acid. The concentration of LTA solution was determined by standard hypo solution. The solutions of the substrate (ketones) were prepared by dissolving the appropriate quantity of the compounds in the same solvent, so that the concentration of the ketones was maintained always higher than the concentration of LTA.

The ketone solution and LTA solutions were thermally equilibrated. Equal volumes (10 ml) of these solutions were pipetted out into a conical flask kept in the thermostat. A stop watch was started when half of the second solution had been delivered. 2 ml aliquots were quenched into 0.1N solution (10 ml) of potassium iodide containing sodium carbonate, treated with 6M (2ml) sulphuric acid and kept in dark for about 10 minutes for complete liberation of iodine, diluted with water and then titrated with a standard solution of sodium thiosulphate from a micro burette using 1% starch as indicator. The hypo solution was standard-

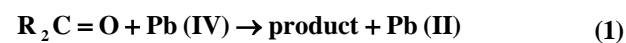
ized by aqueous dichromate solution. The disappearance of blue color is the end point of the titration. From the titre value the amount of LTA reacted was calculated.

#### Product analysis

For the oxidation of ketones by LTA the ketones were dissolved in 25 ml of 98% acetic acid and treated with LTA solution. The concentration of LTA was maintained in excess than the concentration of the ketone. The resulting mixture was kept aside at room temperature for 1 day. After that, all the acid was removed under vacuum and the compound extracted with ether and dried over anhydrous sodium sulphate. The product was isolated after removing ether.

#### Stoichiometry

The stoichiometry of the reaction was determined by allowing a known excess of the oxidant LTA to react with the substrate in glacial acetic acid medium at 30°C and estimating the unreacted LTA. The stoichiometry was found to be in the mole ratio of 1:1 for oxidant to substrate.



#### Calculation of rate constants

The rate constants of all the reactions were calculated by using the second order integrated rate equation.

$$k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad (2)$$

where, a = initial concentration of ketone in moles / litre; b = initial concentration of Pb (IV) in moles / litre; x = amount of Pb (IV) reacted in time 't' see.

### RESULTS AND DISCUSSION

The kinetic studies on the oxidation of the ketones prepared 2-aryl-trans-decahydroquinolin-4-ones (1 to 8) was carried out by using LTA as oxidant in acetic acid (98%) medium. The reaction was found to follow over all second order, first order each in substrate and oxidant. The rate constants for the different substrates were given in TABLE-1. An examination of the rate constants for the oxidation of 2-aryl-trans-decahydroquinolin-4-ones (1 to 3, where there is no methyl group at 3<sup>rd</sup> posi-

tion) with those of corresponding 3-Methyl-2-aryl-*trans*-decahydroquinolin-4-ones (4,5 and 6, where there is methyl group at 3<sup>rd</sup> position) reveal that the latter series of compounds i.e. 4,5 and 6 were oxidized at a much slower rate than former series of compounds 1 to 3. The same trend was reported by satyanarayana in the oxidation of the same compounds with Tl (III)<sup>[15]</sup> and Ce (IV)<sup>[16]</sup> as oxidants in aqueous acetic acid.

**TABLE 1 : Second order rate constants of the oxidation of substituted 2-aryl-*trans*-decahydroquinolin-4-ones by LTA.**

Solvent = 98% AcOH; Temperature = 30°C;

S.No.	Compound	$k_2 \times 10^2, \text{Mole}^{-1} \text{Sec}^{-1}$
1.	2-ph-4-one	11.42 ± 0.05
2.	2-( <i>p</i> -tolyl)-4-one	13.48 ± 0.15
3.	2-( <i>p</i> -OMe)-4-one	15.12 ± 0.11
4.	3-Me-2-ph-4-one	03.78 ± 0.15
5.	3-Me-2- <i>p</i> -tolyl-4-one	03.66 ± 0.07
6.	3-Me-2-( <i>p</i> -OMe)-4-one	00.79 ± 0.02
7.	1,3-di-Me-2-ph-4-one	03.55 ± 0.21
8.	2- <i>o</i> -Cl-Ph-4-one	17.40 ± 0.16

The effect of 3-methyl substituent might be attributed to the steric approach of the reagent in the transition state and also at 3<sup>rd</sup> position the hydrogen atom become less acidic and hence the rate of oxidation of these compounds (4, 5 and 6) are lower than those of compounds 1 to 3. The kinetic study<sup>[15]</sup> of Tl (III) on the present compounds shows (TABLE 2) that the compound 7 i.e. 1,3-dimethyl-2-phenyl-*trans*-decahydroquinolin-4-one was oxidized at a much faster rate when compared with the rates of oxidation of compound (1), having no methyl group in position 3 or compound (4), having methyl group at position 3. But, it was found that the rate of oxidation compound 7 in the present investigation with Pb (IV) was low when compared to the compounds 1 and 4, having no methyl group in position 3 and having methyl group at position 3 respectively. Further, the rate of oxidation of 2-*o*-chlorophenyl-*trans*-decahydroquinolin-4-one (8) was found to be abnormally high when compared with the rates of oxidation of compounds 1 to 6. This observation is similar to the observation made by satyanarayana<sup>[15]</sup> with Tl (III) and quite contrary to the observation made by Vimala Devi<sup>[19]</sup> while studying the oxidation of 2,6-diaryl-4-piperidones with N-bromosuccinimide.

**TABLE 2 : Second order rate constants of the oxidation of 2-aryl-*trans*-decahydroquinolin-4-ones by thallium(III)\*.**

Temp.= 30°C; [H<sup>+</sup>] = 4.0 N; Solvent = 80% AcOH

Sl.No.	Compound	$k_2 \times 10^3 \text{dm}^3 \text{mole}^{-1} \text{sec}^{-1}$
1	2-ph-4-one	8.44 ± 0.09
2	2-( <i>p</i> -tolyl)-4-one	8.47 ± 0.13
3	2-( <i>p</i> -OMe)-4-one	11.22 ± 0.01
4	3-Me-2-ph-4-one	1.39 ± 0.04
5	3-Me-2- <i>p</i> -tolyl-4-one	1.44 ± 0.01
6	3-Me-2-( <i>p</i> -OMe)-4-one	0.93 ± 0.04
7	1,3-di-Me-2-ph-4-one	30.40 ± 0.03
8	2- <i>o</i> -Cl-Ph-4-one	24.98 ± 0.04

\*= Ch. Vijayasradhi, et.al., Oxidation Communications, Vol. 33(2), 371(2010).

The introduction of electron releasing and electron withdrawing substituents in the aryl group at *ortho*- and *para*- positions was given better understanding of relation between structure and reactivity. Substitution at *ortho*- and *para*- positions of aryl ring is expected to produce some what little effect on the rate of oxidation, because aryl ring is far away from the reaction centre. But the substituents at *ortho*- and *para*- positions played a vital role on oxidation rate. This is mainly due to the polar effect exerted by the substituents. The electron releasing groups increased the rate of oxidation. This gains evidence from the observation that *p*-methoxyphenyl-*trans*-decahydroquinolin-4-one (3) was found to oxidize faster than the unsubstituted compound (1, TABLE 1) and the rate of oxidation of *p*-OMe-ketone (3, TABLE 1) was higher than any other ketones 1-7 except 8 under present investigation.

Moreover the rate of oxidation of 2-(*p*-OMe)-2-phenyl-*trans*-decahydroquinolin-4-one was found to be high when compared with the rates of oxidation of compounds 1 and 2 and this trend was also similar in respect of the reagents Tl (III) (TABLE 2) and Ce (IV) (TABLE 3) in the oxidation of the same compounds.

The oxidation kinetics was carried out by varying the temperature and the results were given in TABLE 4. With increasing in the temperature the rate of oxidation was found to increase.

### Product analysis and mechanism of oxidation

The product analysis of the compounds was done as given in experimental part. The completion of the

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reaction was confirmed by comparison of T.L.C. of starting material with reaction mixture. But the product obtained was not giving a particular mass; it may be of mixture of product and reactant. For this reason the reaction mixture was run down on different type's columns to separate the product mixture.

**TABLE 3 : Second order rate constants of the oxidation of 2-aryl-trans-decahydroquinolin-4-ones by Ce(IV)\*.**

Temp. 35°C; [H<sup>+</sup>] = 4.0 N; Solvent = 50 % AcOH

Sl.No.	Compound	k <sub>2</sub> x 10 <sup>3</sup> dm <sup>3</sup> , mole <sup>-1</sup> sec <sup>-1</sup>
1	2-ph-4-one	1.19 ± 0.04
2	2-(-p-tolyl)-4one	1.07 ± 0.02
3	2-(p-OMe)-4one	1.23 ± 0.01
4	3-Me-2-ph-4one	0.25 ± 0.12
5	3-Me-2-p-tolyl-4one	0.03 ± 0.02

\*= Satyanarayana P.V.V., et.al., Oxidation Communications, vol.36(1, ) 2013(Inpress).

**TABLE 4 : Effect of temperature on rate of oxidation of 2-Phenyl-trans-decahydroquinolin-4-one by Pb(IV).**

Solvent = 98%AcOH

Temperature(°C)	k <sub>2</sub> x 10 <sup>2</sup> , Mole <sup>-1</sup> . Sec <sup>-1</sup>
30	11.42 ± 0.05
35	17.11 ± 0.25
40	25.72 ± 0.32
45	36.64 ± 0.15

A serious attempt was made to isolate the product obtained on the oxidation of the compound 1 (3-H) and 5 (3-CH<sub>3</sub>). Under the reaction conditions the reaction was found to proceed smoothly and the oxidizing agent was consumed. On working up the reaction mixture gave a product while was found to be the starting material. But the recovery of the reactant was found to be less than the amount taken initially. This observation made the author to think that probably the product may be an amino acid, which is soluble in water during working-up the reaction mixture and only the reactant could be recovered. This gains support from the observation made by Meenal<sup>[20]</sup> and Dhar<sup>[21]</sup> in that they reported the possible formation of amino acid in the oxidation of 2,6-diaryl-4-piperidones. A similar observation was also made by satyanarayana<sup>[15,16]</sup> for the oxidation of same compounds with Tl (III) and Ce (IV). From these observations the possible products are

As it was not become possible to isolate the product, an attempt was also made to isolate the products

by using reverse phase column (resin columns) by elution with different proportions of methanol and water. After that the solvent was removed under high vacuum to recover the product.

An examination of the IR and Mass spectra of the products revealed that they are quite different from the spectra of the original compounds taken. The broad peak (3424 cm<sup>-1</sup>) in the region of 3300-3450 cm<sup>-1</sup> indicated the presence of -OH group, which may be the -OH group of carboxylic acid. This supported the assumption of the product aminoacid (Figure 2 & 3). However, no definite conclusion was obtained in establishing complete structure of the products.

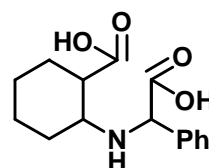


Figure 2: Product of compound 1

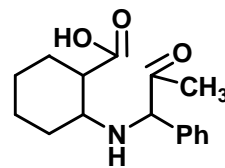
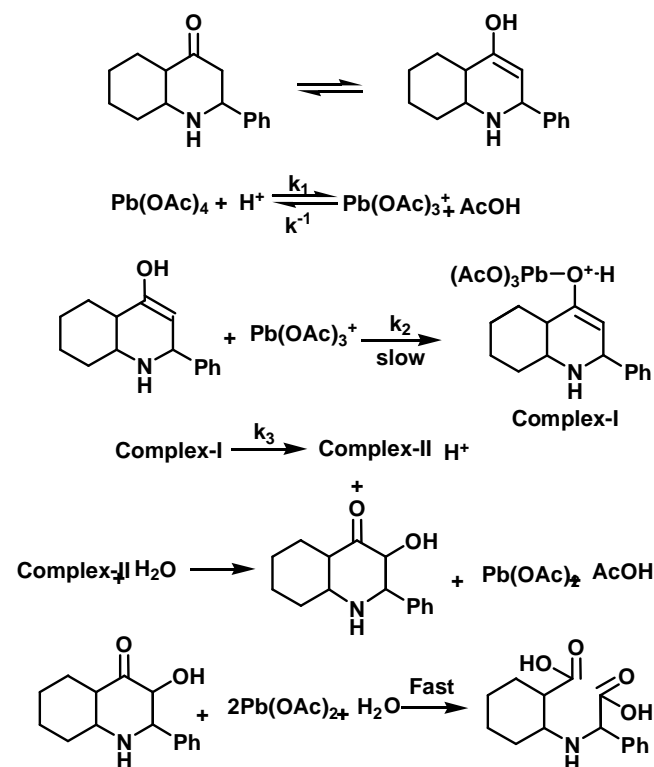


Figure 3: Product of compound 5



However the proposed mechanism is similar to mechanism obtained in the oxidation<sup>[22]</sup> of 2,6-diaryl-4-piperidones with LTA. Basing on this formation of aminoacid assumption a suitable mechanism has been proposed (scheme 1).

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