



**CETYLTRIMETHYLAMMONIUM DICHROMATE OXIDATION OF  
2-ARYL-TRANS-DECAHYDROQUINOLIN-4-OLS: A KINETIC, MECHANISTIC  
AND CONFORMATIONAL STUDY BY SPECTROPHOTOMETRIC APPROACH**

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**Abstract:** A new and selective oxidant Cetyltrimethylammonium dichromate (CTADC) was utilized for the oxidation of substituted *trans*-decahydroquinolin-4-ols in order to study the mechanism of oxidation and to identify the possible products of the oxidation. The oxidation studies were carried out in presence of aqueous acetic acid medium containing small amount of sulphuric acid (6 N). The course of the reaction was followed spectrophotometrically. The order of the reaction was found to be second order both by rate equation and graphical method. Axial alcohols were found to get oxidized at a much faster rate than equatorial alcohols and alcohols having a methyl group at position 3 of the decalin ring system were also found to oxidize at a faster rate unlike with other metal ion oxidants. Substituents on phenyl ring at position 2 of decalin ring were found to influence the rate of oxidation of alcohols. The rates of oxidation of 3-methyl-2-aryl-*trans*-decahydroquinolin-4-ols were also carried out by varying the parameters like temperature, acid strength and solvent composition.

**Key words:** Decahydroquinolin-4-ols, CTADC, Oxidation, Mechanism, Conformational analysis.

### Introduction

Kinetics of oxidation of secondary alcohols had been studied extensively<sup>i-v</sup> by various workers using different oxidizing agents. Particularly the chromium (VI) reagents are highly valuable oxidizing agents in organic chemistry<sup>vi,vii</sup>. Chromium trioxide, potassium and sodium dichromates have long been used for the oxidation of organic substrates. But these reagents were not suitable oxidizing agents for complex and acid sensitive compounds. To surmount these difficulties Collin's reagent<sup>viii</sup>, Corey's reagent<sup>ix</sup>, Pyridinium dichromate<sup>x</sup>,

4-(N,N-dimethylamino)-pyridinium chlorochromate<sup>xi</sup>, nicotinium dichromate<sup>xii</sup>, 2,2'-bipyridinium chlorochromate<sup>xiii</sup>, triethylammonium chlorochromate<sup>xiv</sup>, Benzyltriethyl-ammonium dichromate<sup>xv</sup>, pyridinium silver dichromate<sup>xvi</sup>, pyridinium chlorochromate on polymer support<sup>xvii</sup> and other halochromates like pyridinium fluorochromate<sup>xviii</sup>, quinolinium fluorochromate<sup>xix</sup>, quinolinium bromochromate<sup>xx</sup>, pyridinium bromochromate<sup>xxi</sup>, tetramethylammonium fluorochromate<sup>xxii</sup>, tributylammonium chlorochromate<sup>xxiii</sup>, tetrapropylammonium bromochromate and tetrabutylammonium bromochromate<sup>xxiv</sup> were used for oxidation of secondary alcohols. However, most of these reagents also suffer with some disadvantage such as instability, difficulty of preparation, requirement of large excess of reagent, hygroscopicity, low selectivity or cost of use and tedious workup procedures. To overcome some of these disadvantages, among the phase transferring reagents, cetyltrimethylammonium dichromate (CTADC) was found to be a new, selective and mild phase transferring oxidant. When treated with CTADC in the presence of dichloromethane and a trace of acetic acid medium, primary and secondary aliphatic, alicyclic alcohols were oxidized to give ketones with good yield<sup>xxv</sup>. As a part of extension of our study on conformations of 2-aryl-*trans*-decahydroquinolin-4-ols<sup>xxvi,xxvii</sup> and to extend use of CTADC for the oxidation of quinolin-4-ols the present investigation was carried out in aqueous acetic acid medium spectrophotometrically.

## Experimental

### Kinetic Measurements

*Preparation of alcohols:* The required alcohols were prepared by the following method developed by Baliah and Natarajan<sup>xxviii</sup>, which involved the preparation of their corresponding ketones followed by reduction with Na/n-butanol, M.P.V. reduction, sodium borohydride reduction and water mediated reduction by sodium borohydride<sup>xxix</sup>. Cetyltrimethylammonium dichromate was prepared by the known method<sup>xxx</sup> and its purity was checked by estimating Cr (VI) iodometrically<sup>xxxi</sup>.

*Purification of Materials:* The alcohols were purified by recrystallization from suitable solvents to constant melting points. All these samples were dried in vacuum before use.

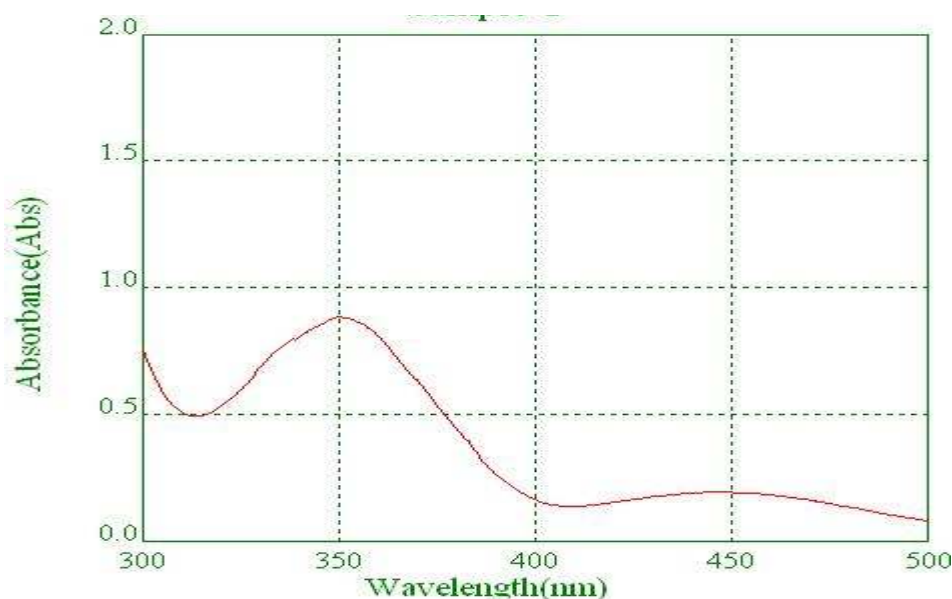
*Acetic Acid:* Acetic acid glacial (Excelar), supplied by 'Qualigens Fine Chemicals', was refluxed with chromium trioxide for 6 h and fractionally distilled. The fraction boiling at 390-391K was collected and used.

*Other Reagents:* Cetyltrimethylammonium bromides, Potassium dichromate, Potassium iodide, Sulphuric acid used were all A.R grade. Doubly distilled water was used for all purposes.

*Instrument:* The instrument used was Analytical technologies UV/visible spectrophotometer of Model Spectro2080.

*Kinetic Procedure:* The oxidation kinetics of 2-aryl-*trans*-decahydroquinolin-4-ols by CTADC in the presence of aqueous acetic acid was investigated by using a UV-Vis

spectrophotometric method and all the kinetic measurements were carried out at 350nm (Figure 1). The measurements were performed in 50:50(v/v) acetic acid: water containing 6N H<sub>2</sub>SO<sub>4</sub> at 30 °C. The temperature was controlled by using thermostat of accuracy ±0.1 °C. The required amount of CTADC solution was prepared by dissolving the necessary amount of CTADC in the solvent medium. The solutions of the substrate were prepared by dissolving the appropriate quantity of the compounds in the same solvent, so that the concentration of the alcohols was maintained always higher than the concentration of CTADC. The reaction was initiated by mixing CTADC to alcohols and the progress of the reaction was followed spectrophotometrically by monitoring the decrease in absorbance at 350 nm. The second order conditions were followed for determining the rates of the reactions.



**Figure 1.** UV-absorption maxima of the CTADC reagent.

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

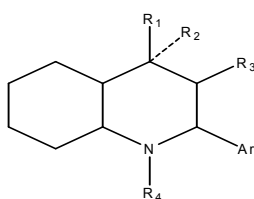
$$k_2 = \log \frac{2.303 \quad b(a-x)}{t(a-b) \quad a(b-x)}$$

Where,

- a= initial concentration of alcohol in moles /litre
- b= initial concentration of CTADC in moles /litre
- x= amount of CTADC reacted in time 't' sec

### Results and Discussion

Oxidation of 2-aryl-*trans*-decahydroquinolin-4-ols (Figure 2) with CTADC in aqueous acetic acid medium was found to be almost negligible. However, the oxidation was found to take place in the presence of the added sulphuric acid. Further the increase in the concentration of added sulphuric acid was found to increase the rate of oxidation. Hence, the concentration of H<sub>2</sub>SO<sub>4</sub> was maintained constant when it was necessary to compare the rate data.



**Figure 2.** 2-Aryl-*trans*-decahydroquinolin-4-ols

No	2-aryl- <i>trans</i> - decahydroquinolin-4-ols (I) R <sub>3</sub> and R <sub>4</sub> = H	No	3-methyl-2-aryl- <i>trans</i> -decahydroquinolin-4-ols (II) R <sub>3</sub> = CH <sub>3</sub> and R <sub>4</sub> = H	No	1-methyl & 1, 3-di- methyl- 2-phenyl- <i>trans</i> -deca-hydro quinolin-4-ols (III) Ar = C <sub>6</sub> H <sub>5</sub> and R <sub>4</sub> = CH <sub>3</sub>
1	Ar = C <sub>6</sub> H <sub>5</sub> , R <sub>1</sub> = OH, R <sub>2</sub> = H	9	Ar = C <sub>6</sub> H <sub>5</sub> , R <sub>1</sub> = OH, R <sub>2</sub> = H	17	R <sub>1</sub> = OH, R <sub>2</sub> = H, R <sub>3</sub> = H
2	Ar = C <sub>6</sub> H <sub>5</sub> , R <sub>1</sub> = H, R <sub>2</sub> = OH	10	Ar = C <sub>6</sub> H <sub>5</sub> , R <sub>1</sub> = H, R <sub>2</sub> = OH	18	R <sub>1</sub> = H, R <sub>2</sub> = OH, R <sub>3</sub> = H
3	Ar = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = OH, R <sub>2</sub> = H	11	Ar = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = OH, R <sub>2</sub> = H	19	R <sub>1</sub> = OH, R <sub>2</sub> = H, R <sub>3</sub> = CH <sub>3</sub>
4	Ar = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = H, R <sub>2</sub> = OH	12	Ar = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = H, R <sub>2</sub> = OH	20	R <sub>1</sub> = H, R <sub>2</sub> = OH, R <sub>3</sub> = CH <sub>3</sub>
5	Ar = <i>o</i> -Cl-C <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = OH, R <sub>2</sub> = H	13	Ar = <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = OH, R <sub>2</sub> = H		
6	Ar = <i>o</i> -Cl-C <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = H, R <sub>2</sub> = OH	14	Ar = <i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = H, R <sub>2</sub> = OH		
7	Ar = <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = OH, R <sub>2</sub> = H	15	Ar = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = OH, R <sub>2</sub> = H		
8	Ar = <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = H, R <sub>2</sub> = OH	16	Ar = <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> , R <sub>1</sub> = H, R <sub>2</sub> = OH		

The rate constants of all the reactions were calculated by using the second order integrated rate equation and the oxidations of all the compounds were found to follow overall second order. The rate constants ( $k_{obs}$ ) were also obtained by using graphical method i.e from the slope of the linear plot of  $2.303/(a-b) \times \log b/a[(a-x)/(b-x)]$  versus time (t) (studied up to 70-80% completion of the reaction) and found to be consistent with the values obtained by second order rate equation. However, for a set of epimeric alcohols (**1&2**) were only presented in Fig. 3&4.

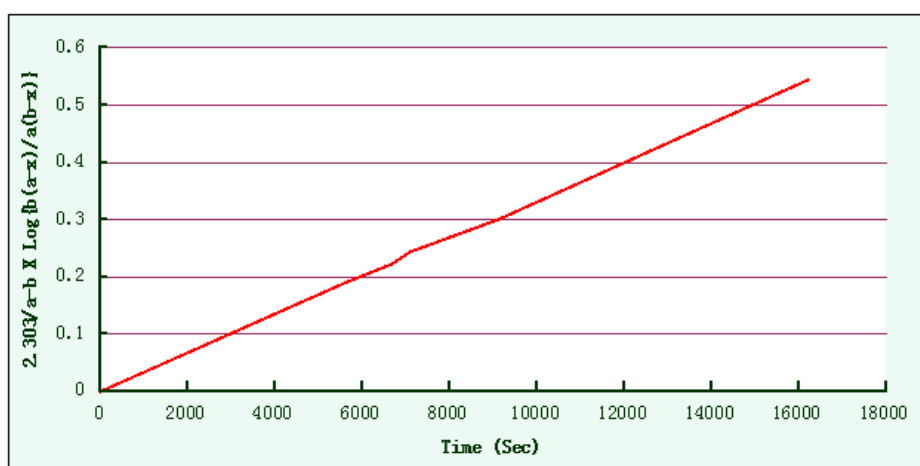
**Evaluation of Rate constant (k) by graphical method:** The rate constants for all the reactions were determined as given below for 2-phenyl-*trans*-decahydroquinolin-4-ol (**1&2**) (Table 1 & 2) and the second order graphs of both linear and non-linear curve fits obtained were given in figures 3(a&b)&4(a&b). The rate constants obtained for all the three groups were reported in the tables 3,5 &6 respectively.

The kinetic data for the oxidation of 2-aryl-*trans*-decahydroquinolin-4-ols (**1 to 8**) (I), 3-methyl-2-aryl-*trans*-decahydroquinolin-4-ols (**9 to 16**) (II), 1-methyl-2-aryl-*trans*-decahydroquinolin-4-ols (**17 and 18**) and 1,3-dimethyl-2-aryl-*trans*-decahydroquinolin-4-ols (**19 and 20**) (III), (Figure 2) were determined as said above and the results were given in Tables 3,4 and 5 respectively.

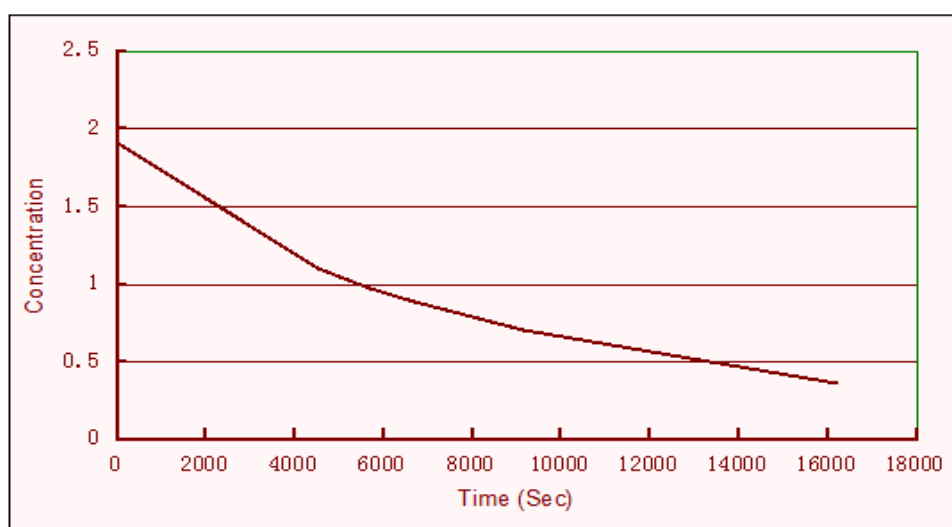
**Table 1.** Determination of second order rate constants for 2-phenyl-*trans*-decahydroquinolin-4-ol (1)

$a = 4.071 \times 10^{-4}$      $b = 1.911 \times 10^{-4}$     AcOH = 50%     $[H^+] = 6N$     Temp = 30 °C

Time (sec)	Absorbance	$b-x \times 10^{-4}$	$a-x \times 10^{-4}$	$b/a[(a-x)/(b-x)]$	$2.303/a-b \times \log b/a[(a-x)/(b-x)]$	$k \times 10^2$
0	0.4302	1.911	4.071	--	0	--
4526	0.2474	1.0990	3.2590	1.3920	0.1531	33.83
5680	0.2192	0.9737	3.1007	1.5107	0.1910	33.63
6698	0.1987	0.8826	3.0426	1.6182	0.2229	33.28
9120	0.1578	0.7010	2.8610	1.9158	0.3010	33.00
16220	0.0825	0.3665	2.5265	3.2359	0.5438	33.53



**Figure 3a.** Linear Plot of  $2.303/a-b \times \log b/a[(a-x)/(b-x)]$  verses time for a second order reaction.

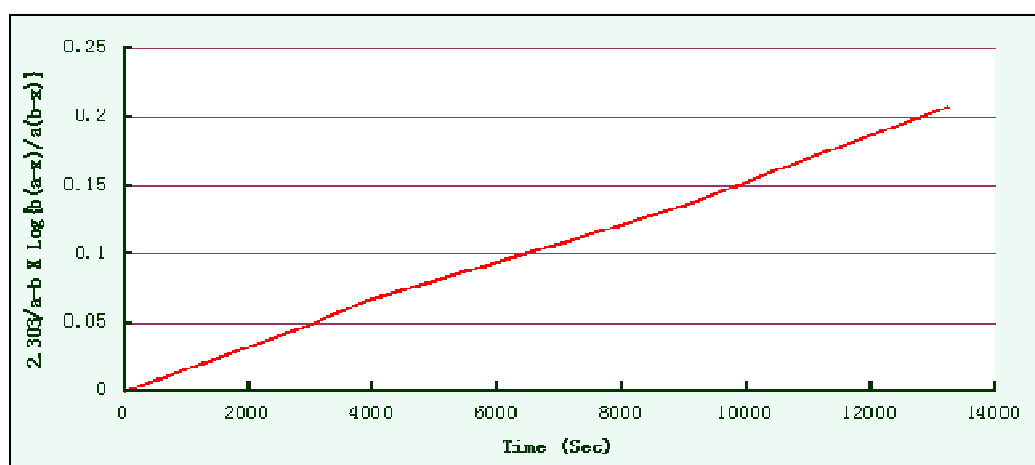


**Figure 3b.** Non-Linear curve fit plot of Concentration verses time for a second order reaction.

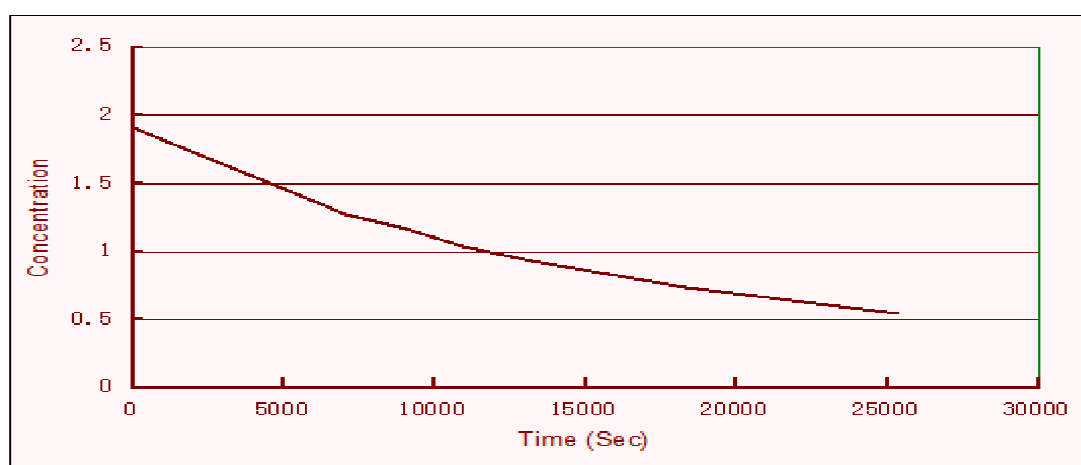
**Table 2.** Determination of second order rate constants for 2-phenyl-*trans*-decahydroquinolin-4-ol) (2)

$a = 4.071 \times 10^{-4}$      $b = 1.911 \times 10^{-4}$     AcOH = 50%     $[H^+] = 6N$     Temp = 30 °C

Time (sec)	Absorbance	b-x X 10 <sup>-4</sup>	a-x X 10 <sup>-4</sup>	b/a[(a-x)/(b-x)]	2.303/a-b X log b/a[(a-x)/(b-x)]	kX10 <sup>2</sup>
0	0.4328	1.911	4.071			
7090	0.2888	1.2752	3.4352	1.2645	0.1087	15.33
9053	0.2634	1.1630	3.3230	1.3412	0.1359	15.01
10970	0.2362	1.0430	3.2030	1.4415	0.1693	15.43
13250	0.2097	0.9259	3.0859	1.5644	0.2072	15.64
18320	0.1681	0.7422	2.9022	1.8355	0.2812	15.35
21050	0.1509	0.6663	2.8263	1.9911	0.3189	15.15
25320	0.1245	0.5497	2.7097	2.3139	0.3885	15.34



**Figure 4a.** Linear Plot of  $2.303/a-b \times \log b/a[(a-x)/(b-x)]$  verses time for a second order reaction.



**Figure 4b.** Non-Linear curve fit plot of Concentration verses time for a second order reaction.

**Table 3.** Second order rate constants for CTADC oxidation of 2-aryl-*trans*-decahydro-quinolin-4-ols.[H<sub>2</sub>SO<sub>4</sub>] = 6N; Solvent: AcOH/H<sub>2</sub>O: 50/50 (v/v), Temp = 30 °C

No	Compound Name	Orientation of OH	k <sub>2</sub> X10 <sup>2</sup> (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	k <sub>ax</sub> /k <sub>eq</sub>
<b>1</b>	2-phenyl- <i>trans</i> -decahydroquinolin-4-ol	a	33.58± 0.13	<b>2.19</b>
<b>2</b>	2-phenyl- <i>trans</i> -decahydroquinolin-4-ol	e	15.32 ± 0.09	
<b>3</b>	2- <i>p</i> -tolyl- <i>trans</i> -decahydroquinolin-4-ol	a	38.18 ± 0.10	<b>2.34</b>
<b>4</b>	2- <i>p</i> -tolyl- <i>trans</i> -decahydroquinolin-4-ol	e	16.30 ± 0.10	
<b>5</b>	2- <i>o</i> -chloro-phenyl- <i>trans</i> -decahydroquinolin-4-ol	a	16.91 ± 0.08	<b>2.03</b>
<b>6</b>	2- <i>o</i> -chloro-phenyl- <i>trans</i> -decahydroquinolin-4-ol	e	08.32 ± 0.11	
<b>7</b>	2- <i>p</i> -methoxy-phenyl- <i>trans</i> -decahydroquinolin-4-ol	a	25.20 ± 0.04	<b>2.19</b>
<b>8</b>	2- <i>p</i> -methoxy-phenyl- <i>trans</i> -decahydroquinolin-4-ol	e	11.47 ± 0.13	

An examination of the rate data (Table 3, 4 & 5) indicated that axial alcohols were found to get oxidized at faster rate than corresponding equatorial alcohols. In most of the epimers the k<sub>ax</sub>/k<sub>eq</sub> ratio is almost greater than 2 which indicate the stability of equatorial alcohols to CTADC reagent than axial alcohols. Further the rates of oxidation of 2-*p*-tolyl-*trans*-decahydroquinolin-4-ols (**3** and **4**) were found to be higher than those of corresponding 2-phenyl-*trans*-decahydroquinolin-4-ols (**1** and **2**) (Table 3). This rate increase was observed in former compounds compared to the later may be attributed due to electron releasing nature of *p*-tolyl group than phenyl group. But the same was not followed when observing the rate data obtained for the oxidation of 2-*p*-methoxyphenyl-*trans*-decahydroquinolin-4-ols (**7** and **8**), the rate of oxidation was found to be less compared to both 2-phenyl and 2-*p*-tolyl systems. This observation was found to be inconsistent with the observation made by Satyanarayana in oxidation with Tl (III)<sup>xxvi</sup>, V (V)<sup>xxvii</sup> and Baliah and Natarajan<sup>xxviii</sup> in the study of oxidation of these alcohols by chromium (VI) ions in aqueous acetic acid medium.

Further, a slight distortion of the chair form of the heterocyclic ring when the phenyl group is replaced by *p*-tolyl group might be responsible for the observed increase in the rate of oxidation of these compounds (**3&4**). Such distortion affects the rates of oxidation of the axial alcohols to a greater extent than the equatorial alcohols. It is pertinent to mention here that while electron-donating groups in phenyl ring increase the rate of oxidation, electron-withdrawing groups decrease the rate of oxidation (compounds **5** and **6**) (Table 3). But in case of 2-*p*-methoxy compounds (**7&8**) the rate of oxidation was less compared to **1-4** compounds may be because of restriction of approach of the reagent to the reaction centre by bulky methoxy group. It is probably attributed to the much higher steric requirement of approach of the reagent and hence lower rates of oxidations were observed.

The introduction of a methyl group in the 3<sup>rd</sup> position of decalin ring was found to increase the rate of oxidation of alcohols (Table 4) through inductive as well as steric effects. However, the rate of oxidation of these compounds was found to decrease with simple metal ions like Tl (III) and V (V) reported by Satyanarayana *et al*<sup>xxvi,xxvii</sup>.

**Table 4.** Second order rate constants for CTADC oxidation of 3-methyl-2-aryl *trans*-decahydro-quinolin-4-ols.[H<sub>2</sub>SO<sub>4</sub>] = 6N; Solvent: AcOH/H<sub>2</sub>O: 50/50 (v/v), Temp = 30°C

No	Compound Name	Orientation of OH	k <sub>2</sub> X10 <sup>2</sup> (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	k <sub>ax</sub> /k <sub>eq</sub>
<b>9</b>	3-methyl-2-phenyl- <i>trans</i> -decahydroquinolin-4-ol	a	38.28± 0.14	<b>2.02</b>
<b>10</b>	3-methyl-2-phenyl- <i>trans</i> -decahydroquinolin-4-ol	e	18.90± 0.09	
<b>11</b>	3-methyl-2- <i>p</i> -tolyl- <i>trans</i> -decahydroquinolin-4-ol	a	60.56± 0.11	<b>1.85</b>
<b>12</b>	3-methyl-2- <i>p</i> -tolyl- <i>trans</i> -decahydroquinolin-4-ol	e	32.71± 0.13	
<b>13</b>	3-methyl-2- <i>p</i> -chloro-phenyl- <i>trans</i> -decahydroquinolin-4-ol	a	27.89± 0.09	<b>1.40</b>
<b>14</b>	3-methyl-2- <i>p</i> -chloro-phenyl- <i>trans</i> -decahydroquinolin-4-ol	e	19.82± 0.06	
<b>15</b>	3-methyl-2- <i>p</i> -methoxy-phenyl- <i>trans</i> -decahydroquinolin-4-ol	a	33.25± 0.12	<b>2.17</b>
<b>16</b>	3-methyl-2- <i>p</i> -methoxy-phenyl- <i>trans</i> -decahydroquinolin-4-ol	e	15.28± 0.09	

The rate of oxidation of **11** and **12** (3-methyl-2-*p*-tolyl-*trans*-decahydroquinolin-4-ol) was higher than any of compounds in the series under investigation. The rates of oxidation of 1-methyl-2-phenyl-*trans*-decahydroquinolin-4-ols (**17**&**18**) and 1,3-dimethyl-2-phenyl-*trans*-decahydroquinolin-4-ols (**19** & **20**) (Table 5) were slightly lower than their corresponding 2-phenyl-*trans*-decahydroquinolin-4-ols (**1**&**2**) (Table 3) and 3-methyl-2-phenyl-*trans*-decahydroquinolin-4-ols (**9** & **10**) (Table 4). The slow reactivity of the former compounds (**17**, **18**, **19** & **20**) than later compounds (**1**, **2**, **9** & **10**) may be due to the slight deformation of the heterocyclic ring when a methyl group was introduced on N-atom and was supported the assumption made by Baliah and Chandrasekharan<sup>xxxiii</sup> while studying Cr (VI) oxidation of 2, 6-diaryl-piperidin-4-ols and Satyanarayana *et al*<sup>xxvi,xxvii</sup> in oxidation of the same compounds with Tl (III) and V (V).

**Table 5.** Second order rate constant for CTADC oxidation of 1-methyl-2-phenyl-*trans*-decahydroquinolin-4-ols[H<sub>2</sub>SO<sub>4</sub>] = 6N; Solvent: AcOH/H<sub>2</sub>O: 50/50 (v/v), Temp = 30°C

No	Compound Name	Orientation of OH	K <sub>2</sub> X10 <sup>2</sup> (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	k <sub>ax</sub> /k <sub>eq</sub>
<b>17</b>	1-Me-2-Ph- <i>trans</i> -decahydroquinolin-4-ol	a	32.28 ± 0.07	<b>2.40</b>
<b>18</b>	1-Me-2-Ph- <i>trans</i> -decahydroquinolin-4-ol	e	13.40 ± 0.10	
<b>19</b>	1,3-di-Me-2-Ph- <i>trans</i> -decahydroquinolin-4-ol	a	40.62 ± 0.08	<b>2.72</b>
<b>20</b>	1,3-di-Me-2-Ph- <i>trans</i> -decahydroquinolin-4-ol	e	14.94 ± 0.04	

The oxidation kinetics of 3-methyl-2-aryl-*trans*-decahydroquinolin-4-ols have also



been carried out in different compositions of acetic acid water mixture and the relevant data was given in Table 6. The concentration of sulphuric acid was maintained constant at 6.0 N in all these studies and the temperature was at 30 °C. Increase in the percentage of acetic acid in the medium increased the rate of oxidation. Further increase in concentration of sulphuric acid also increased the rate of oxidation of the said compounds and the data was given in the Table 7. An increase in the polarity and decrease in the hydrophobicity of the medium increased the rate of the reaction.

**Table 6.** Effect of solvent composition on the oxidation of 3-methyl-2-aryl-*trans*-decahydroquinolin-4-ols by CTADC.

[H<sub>2</sub>SO<sub>4</sub>] = 6N; Temp = 30 °C

Name of the Compound	Percentage of Acetic acid (10 <sup>2</sup> X k <sub>2</sub> dm <sup>3</sup> mol <sup>-1</sup> sec <sup>-1</sup> )		
	40%	50%	60%
3-Methyl-2- <i>p</i> -tolyl-decahydroquinolin- <i>trans</i> -4-ol (12)	20.23±0.13	32.71±0.05	75.33±0.52
3-Methyl-2- <i>p</i> -tolyl- <i>trans</i> -decahydroquinolin-4-ol (11)	23.41±0.03	60.56±0.19	141.26±0.58

**Table 7.** Effect of [H<sup>+</sup>] on the oxidation of 3-methyl-2-aryl-*trans*-decahydroquinolin-4-ols by CTADC.

Solvent: AcOH/H<sub>2</sub>O: 50/50 (v/v), Temp = 30°C.

Name of the Compound	Variation in [H <sup>+</sup> ] (10 <sup>2</sup> X k <sub>2</sub> dm <sup>3</sup> mol <sup>-1</sup> sec <sup>-1</sup> )		
	5N	6N	7N
3-Methyl-2- <i>p</i> -tolyl-decahydroquinolin- <i>trans</i> -4-ol(12)	32.51 ± 0.22	32.71 ± 0.05	61.65 ± 0.23
3-Methyl-2- <i>p</i> -tolyl- <i>trans</i> -decahydroquinolin-4-ol(11)	46.30 ± 0.35	60.56 ± 0.19	101.22 ± 1.01

The oxidation studies were also carried out at different temperatures (Table 8), with an increase in temperature, the rate constants were found increased.

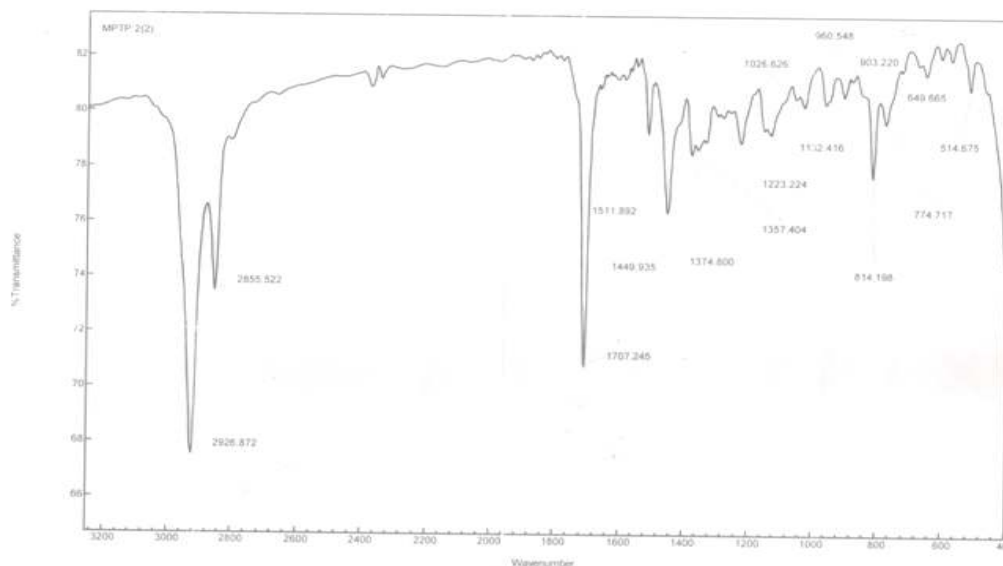
**Table 8.** Effect of temperature on the oxidation of 3-methyl-2-aryl-*trans*-decahydro-quinolin-4-ols by CTADC.

[H<sub>2</sub>SO<sub>4</sub>] = 6N Solvent: AcOH/H<sub>2</sub>O: 50/50 (v/v).

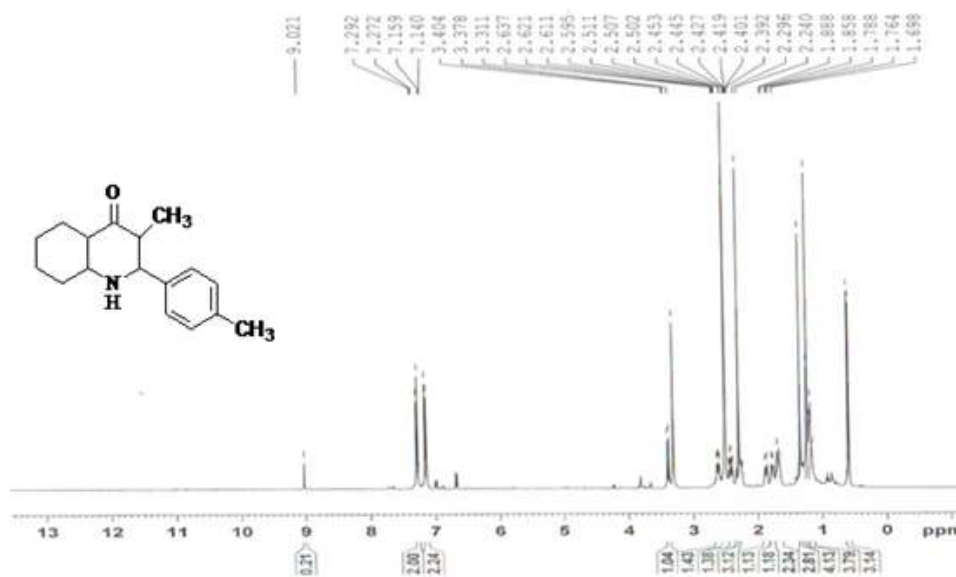
Name of the Compound	Variation in temperature (10 <sup>2</sup> X k <sub>2</sub> dm <sup>3</sup> mol <sup>-1</sup> sec <sup>-1</sup> )		
	30°C	40°C	50°C
3-Methyl-2- <i>p</i> -tolyl-decahydroquinolin- <i>trans</i> -4-ol(12)	32.71 ± 0.05	61.60 ± 1.12	71.54 ± 1.15
3-Methyl-2- <i>p</i> -tolyl- <i>trans</i> -decahydroquinolin-4-ol(11)	60.56 ± 0.19	144.16 ± 0.09	186.25± 0.09

**Product Analysis:** A mixture of alcohol and CTADC was allowed to react in aqueous acetic acid (50%, v/v) in presence of sulphuric acid (6.0N). The concentration of CTADC was maintained higher than the concentration of alcohols. The resulting mixture was kept aside at 30 °C temperature for about two days. The mixture turned to reddish green, indicating the formation of reduced Cr(III). The mixture was then treated with 10% NaOH solution in order to make the solution becomes slightly basic nature, extracted with chloroform. A crude product was obtained after distillation of the chloroform layer. Later it was subjected to

column chromatography for further purification with Hexane: Ethyl acetate in 6:4 ( $R_f=0.5$ ). Finally the product was confirmed by IR &  $^1\text{H NMR}$  (Figure 5 & 6). Hence the oxidation of decahydroquinolin-4-ols by CTADC gave their corresponding ketones. A similar observation was also reported<sup>xxv</sup> in the oxidation of alicyclic alcohols to ketones.



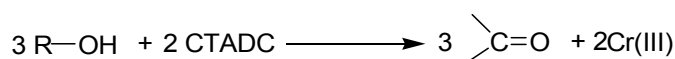
**Figure 5.** IR spectrum of product of 3-methyl-2-*p*-tolyl-*trans*-decahydroquinolin-4-ols.



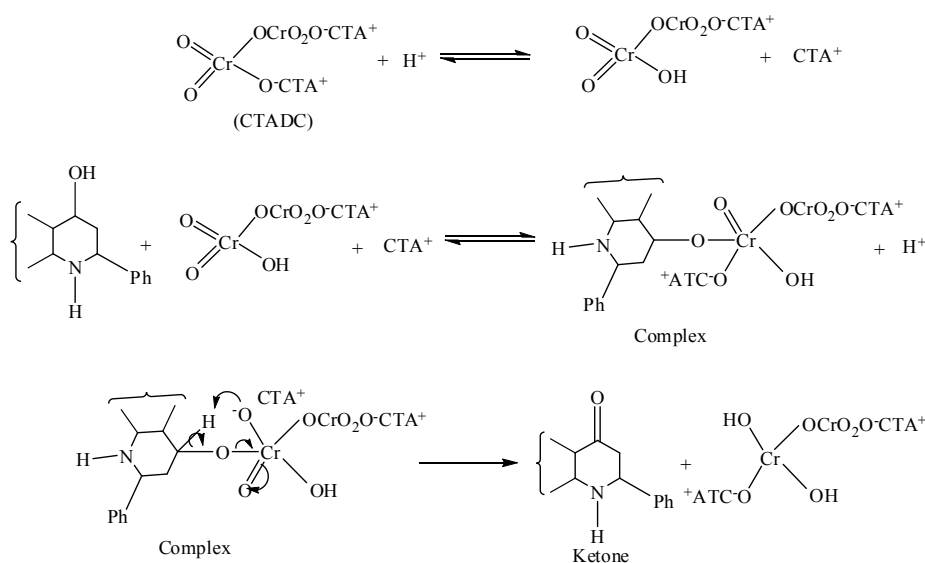
**Figure 6.**  $^1\text{H NMR}$  spectrum of product of 3-methyl-2-*p*-tolyl-*trans*-decahydroquinolin-4-ols.

**Stoichiometry:** The stoichiometry of the reaction was determined by performing the experiment at 30 °C. A number of reaction mixtures containing excess of CTADC than alcohols were kept in a thermostat at 30 °C for 12 hours at varying concentrations of CTADC. The disappearance of Cr(VI) was followed, until the absorbance values become constant and was found that 2 moles of the reagent was utilized for 3 moles of alcohol. The stoichiometric

equation can be written as,



**Mechanism of Oxidation:** Consistent with the above product analysis and stoichiometric observations, the proposed mechanism (scheme 1) involves the following steps. The protonation of dichromate is the initial step of the reaction. The formation of a complex between alcohol and the protonated dichromate is the slow step of the reaction i.e. the rate determining step. Finally, the complex rapidly decomposes to the corresponding ketone in the final step. A similar mechanism was also reported<sup>xxv</sup> in the oxidation of cyclic alcohols to ketones with CTADC oxidant.



**Scheme 1.** Mechanism of oxidation of 2-aryl-*trans*-decahydroquinolin-4-ol by CTADC.

## Conclusions

A new and selective oxidant CTADC was found to be useful for the oxidation of substituted 2-aryl-*trans*-decahydroquinolin-4-ols. The mechanism of oxidation and possible products of the oxidation was also studied. The overall order of the reaction was found to be second order and axial alcohols were found to get oxidized at a much faster rate than equatorial alcohols. The alcohols having a methyl group at position 3 of the decalin ring system and substituents on phenyl ring at position 2 of decalin ring were found to influence the rate of oxidation of alcohols.

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