

# A KINETICS APPROCH FOR OXIDATION OF P-METHYL BENZHYDROL BY N-CHLOROSUCCINIMIDE

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## Abstract

Kinetic investigations in Keggin-type phosphotungstic acid catalyzed oxidation of p-methyl benzhydrol by N-Chlorosuccinimide in aqueous acetic acid medium. In absence of mineral acids, the oxidation kinetics of p-methyl benzhydrol by N-Chlorosuccinimide in presence of Phosphotungstic acid shows a first order dependence on N-Chlorosuccinimide and fractional order on p-methyl benzhydrol and PTA. Activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperature. A mechanism involving transfer of hydride ion in rate determining step is suggested.

**Key Words:** Acid, Kinetics, oxidant, effect and parameters.

## Introduction

In the recent years, studies of oxidation of various organic compounds by heteropoly acids and Polyoxometalates especially those with Keggin-type structure under homogeneous and heterogeneous reaction conditions<sup>1-9</sup> have attracted considerable attention of the researchers. Literature survey reveals at phosphotungstic acid due to its thermal stability, acidity make it efficient and eco-friendly catalyst in Oxidation of organic compounds such as aromatic amines<sup>10</sup> aromatic alcohols<sup>11</sup>, allylalcohols<sup>12</sup>, styrene<sup>13</sup>, oximes<sup>14</sup> etc. The kinetics of oxidation of benzhydrol by organic halo chromates such as Benzyltriethyl ammonium Chlorochromate<sup>15</sup>, Quinoxalinium bromochromate<sup>16</sup>, Quinolium bromochromate<sup>17</sup>, Pyridinium bromochromate<sup>18</sup>, Tetrabutylammonium tribromide<sup>19</sup> etc have been studied earlier. A number of reports on kinetic studies of

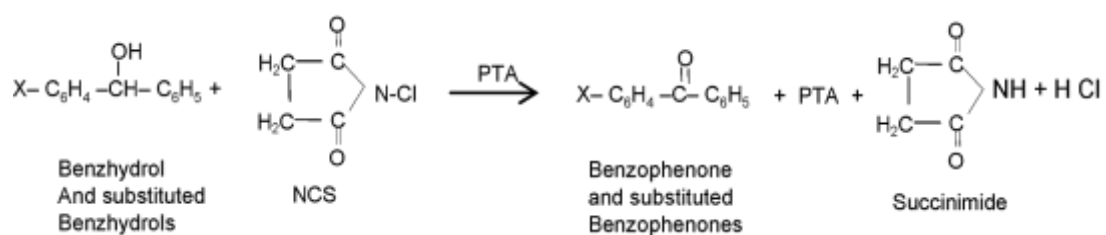
oxidation of benzhydrol with variety of N-halo compound such as N-bromosuccinimide<sup>20</sup>, N-bromosaccharin<sup>21</sup>, N-bromoacetamide<sup>22</sup> and Chloramine-T<sup>23</sup> as oxidants have been reported. N-Chlorosuccinimide is potential oxidizing agent<sup>24-25</sup> and it seems that there are no reports about the kinetics of oxidation of benzhydrol by N-Chlorosuccinimide. The present work reports kinetics and mechanism of PTA catalyzed oxidation of p-methyl benzhydrol by N-Chlorosuccinimide in 30 % acetic acid.

## Materials and method

P-methyl Benzhydrol were prepared by the sodium borohydride reduction of corresponding p-methyl benzophenones. Purity of p-methyl benzhydrol was checked by TLC and M.P. The oxidant N-Chlorosuccinimide (Aldrich sample) was used. Acetic acid (A.R. Grade) was purified by the literature procedure. The standard solutions of p-methylbenzhydrol were prepared in acetic acid. Double stander distilled water was employed in all kinetic runs. To prevent photochemical effect, the freshly prepared solution of N-Chlorosuccinimide was stored in an amber colored bottle and its strength was checked iodometrically using 1 % solution of freshly prepared starch as an indicator.

## Stoichiometry and product analysis

The stiochiometric studies of phosphotugstic acid catalysed p-methyl benzhydrol NCS system at experimental temperature revealed that for each mole of substrate, one mole of oxidant is consumed. The stoichimetric equation can therefore empirically be written as:



Where- PTA=  $H_3PW_{12}O_{40}$  (phosphotungestic acid)

X=P-methyl benzhydrol

The oxidation products p-methyl benzophenone corresponding to substracts were identified for each oxidation qualitatively and chromatographically. The study discards completely the formation of free radicals by the addition of olefinic acrylonitrile (monomer) to the system understudy. The non-occurrence of turbidity and while precipitate rule out polymerization. Similar views were also reported by the oxidation carried out with oxidant  $V(V)^{26}$  and iodate<sup>27</sup> in the above mentioned studies.

## Results and Discussion

The order of reaction with respect to substrate was investigated by varying the five-fold concentration of substrate at constant concentration of oxidant, solvent composition, PTA and temperature. The first-order rate constant increases with increase in substrate concentration. The value of rate constant does not show constancy Table:-I. The plot of  $k^1$  versus [substrate] for substrate is linear initially passing through origin and then bends towards the X-axis (Fig.-I) at higher concentration of substrate. It provides an evidence for the formation of complex between oxidant and substrate. The trend of plot suggests that the reaction rates which follow nearly first-order kinetics with respect to low concentration of substrate and tends to be of zero order showing limiting value at higher concentration of substrate.

**Table: I**

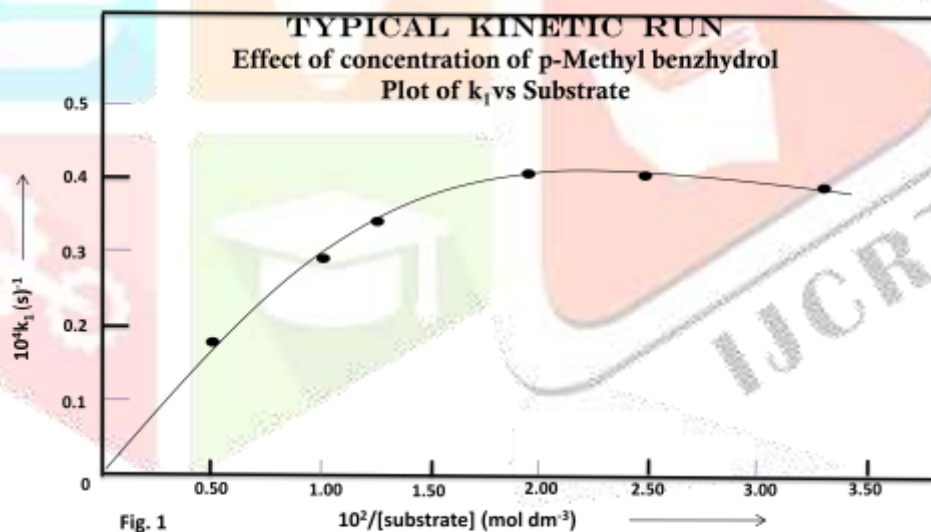
**Dependence of rate on the variation of the concentration of  
p-methylbenzhydrol**

[NCS]	=	$2.50 \times 10^{-3}$ (mol dm <sup>-3</sup> ) ;
[PTA]	=	$2.50 \times 10^{-4}$ (mol dm <sup>-3</sup> ) ;

HOAc-H<sub>2</sub>O = 30% (v/v);

Temp. = 303 °K

SN	10 <sup>2</sup> × [p-methyl Benzhydrol] (mol dm <sup>-3</sup> )	10 <sup>4</sup> k <sub>1</sub> (s <sup>-1</sup> )	10 <sup>-2</sup> / [p-methyl Benzhydrol] (mol dm <sup>-3</sup> )	10 <sup>-4</sup> /k <sub>1</sub>	100k <sub>2</sub> = k <sub>1</sub> /[p-methyl benzhydrol] (mol <sup>-1</sup> sec <sup>-1</sup> )
1	0.50	1.25	2.00	0.800	2.50
2	1.00	2.17	1.00	0.460	2.17
3	1.25	2.41	0.80	0.369	1.92
4	2.00	3.66	0.50	0.273	1.83
5	2.50	3.55	0.40	0.284	1.40
6	3.33	3.45	0.30	0.289	1.00



[NCS] = 2.50 10<sup>-3</sup> × (mol dm<sup>-3</sup>);  
 [PTA] = 2.50 10<sup>-4</sup> × (mol dm<sup>-3</sup>);  
 HO-Ac-H<sub>2</sub>O = 30 % (v/v);  
 Temp. = 303 °K

Similar complex kinetic has also been reported by oxidation of above substrate with NBP<sup>28</sup>. The order of reaction with respect to PTA catalyst was determined by varying the concentration of PTA at constant concentration of oxidant, solvent composition and

temperature. The reaction is PTA catalyzed within a limit. The plot of  $k_1$  vs. [PTA] is obtained linear with passing through the origin in lower concentration, but it bends towards x-axis at higher concentration, indicating fractional order dependence of rate on [PTA].

The order with respect to the p-methyl benzhydrol varies from one to zero showing fraction order. There is kinetic evidence for the rigid intermediate complex formation between oxidant and p-methyl benzhydrol in a pre-equilibrium step at transition state.

**Table : 2**

**Dependence of rate on the concentration of reactant product succinimide**

[NCS]	=	$2.50 \times 10^3$ (mol dm <sup>-3</sup> );
[Substrate]	=	$2.00 \times 10^2$ (mol dm <sup>-3</sup> );
[PTA]	=	$2.50 \times 10^4$ (mol dm <sup>-3</sup> );
HOAc-H <sub>2</sub> O	=	30% (v/v);
Temp.	=	303 <sup>o</sup> K

S.N.	[Succinimide] × 10 <sup>3</sup> (mol dm <sup>-3</sup> )	p-methylBenzhydrol 10 <sup>4</sup> k <sub>1</sub> (s <sup>-1</sup> )
1	0.00	3.66
2	0.50	3.64
3	1.00	3.58
4	1.25	3.46
5	2.00	3.02
6	2.50	2.89

The negligible salt effect shows that the rate determining step involves either neutral species or an ion and a neutral molecule.<sup>29,30</sup> Hence the effect of concentration of succinimide on the oxidation of p-methylbenzhydrol was studied by adding varying concentration of succinimide. From Table: 2. It is evident that with increasing

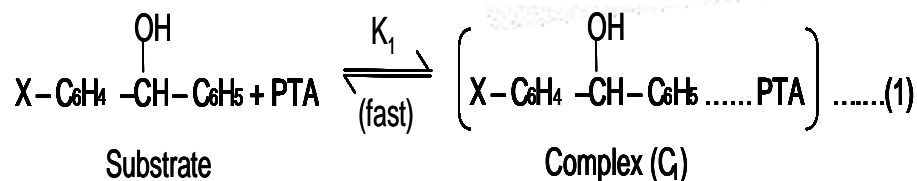
concentration of added succinimide, the rate of oxidation of p-methyl benzhydrol decreases. The plot of  $k^{-1}_1$  Vs. [succinimide] is obtained linear for p-methylbenzhydrol.

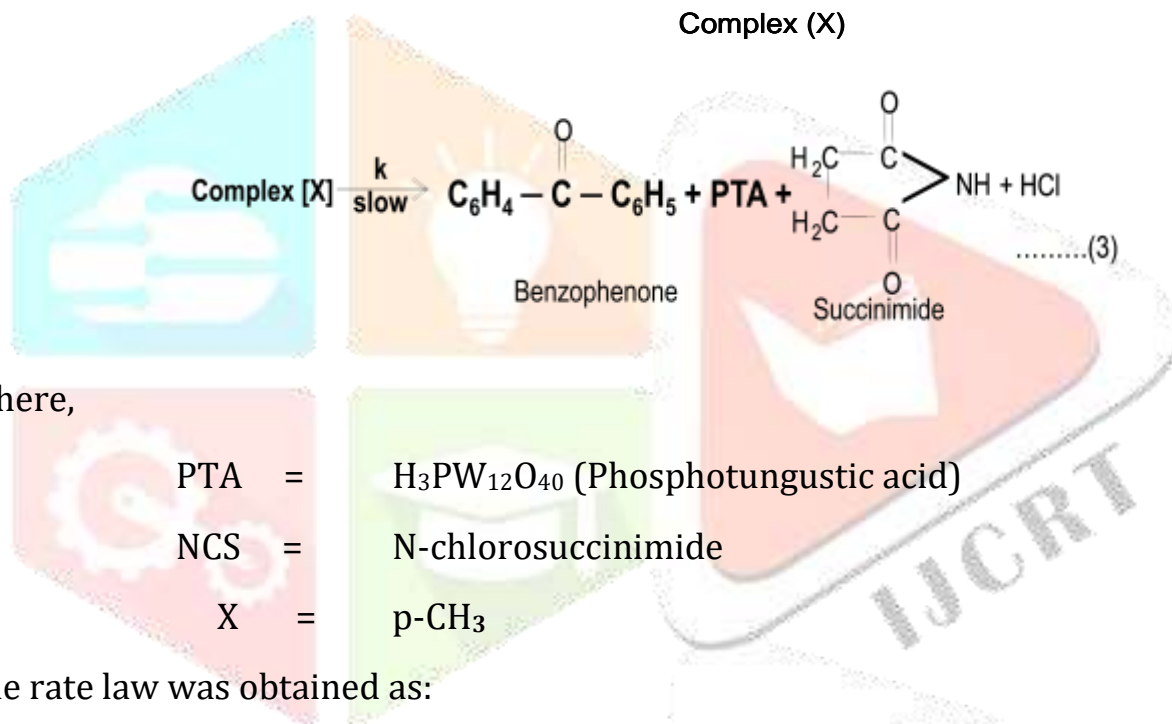
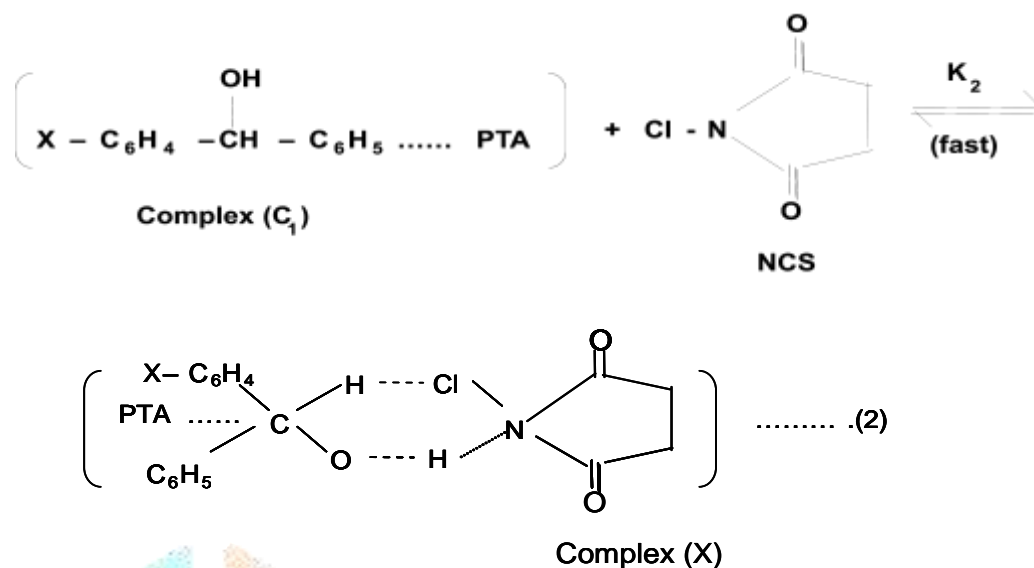
The first- order rate constant decreases with increasing composition of acetic acid - H<sub>2</sub>O i.e. rate slightly decreases with increasing in dielectric constant of the medium. The plot of  $\log k_1$  verses  $10^3/D$  were obtained linear with negative slope in each substrate.

It has been observed that addition of little amounts of Cu<sup>2+</sup> accelerates the reaction rate in all the cases while added Mn<sup>2+</sup> ions have been found to retard the oxidation rate.

There was no significant change in rate constant was observed with variation of H<sup>+</sup> ion. It was found that the ionic strength of the reaction medium has negligible effect on the reaction rate<sup>31</sup>. The addition of primary salts such as NaCl and KCl almost show negligible salt effect on the reaction rate.

Variation of Phthalimide, one of the products of oxidation, had negligible effect on the rate of reaction. The oxidation reactions of p-methylbenzhydrol with N-Chlorosuccinimide catalyzed by PTA at different initial concentrations of acrylonitrile have been investigated. The reaction neither induces polymerization nor retards the reaction rate which may be attributed to the inertness shown by free radicals. Based upon the experimental observation the most probable mechanism has been explained as follows:





Where,

PTA = H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (Phosphotungstic acid)

NCS = N-chlorosuccinimide

X = p-CH<sub>3</sub>

The rate law was obtained as:

$$k' = \frac{k K_2 K_1 [\text{PTA}] [\text{S}]}{1 + K_1 [\text{S}] + K_1 K_2 [\text{S}]}$$

The existed domancy of steric, inductive, hyper-conjugative and mesomeric effects among the molecules are the main reasons of above order of reactivity.

## Conclusion

Kinetic studies utilizing NCS as an oxidant in series of reaction leads us to conclude that the activity of this oxidant is limited and needs to be explored in a laboratory. It

possesses vital potentiality with two electron system and displays interesting behaviours of moderate condition of temperature.

Fruitful outcome of the kinetic studies can be suitably be applied in the field of pharmacology, Hi- tech ,bio chemistry, bio technology in finding the rate of growth of tissues<sup>32</sup> malignancy,<sup>33</sup> and in pharmaco-dynamics.

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