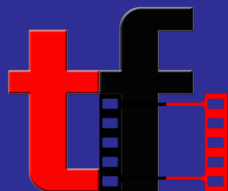


"PHOSPHOTUNGSTIC ACID CATALYZED KINETICS OF OXIDATION OF
BENZHYDROL BY N-CHLOROSUCCINIMIDE IN AQUEOUS ACETIC ACID MEDIUM"



Abstract : Kinetic investigations in Keggin-type phosphotungstic acid catalyzed oxidation of benzhydrol by N-Chlorosuccinimide (NCS) in aqueous acetic acid. In absence of mineral acids, the oxidation kinetics of benzhydrol by NCS in presence of PTA (Phosphotungstic acid) shows a first order dependence on NCS and fractional order on 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.

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Key Words: Benzhydrol, Kinetics, Oxidation, acidity,
homogeneous.

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 conditions¹⁻⁹ have attracted considerable attention of the researchers. Literature survey reveals that phosphotungstic acid (PTA) due to its thermal stability, acidity makes it efficient and eco-friendly catalyst in

Oxidation of organic compounds such as aromatic amines¹⁰ aromatic alcohols¹¹, allyl alcohols¹², styrene¹³, oximes¹⁴ etc. The kinetics of oxidation of benzhydrol by organic halo chromates such as Benzyltriethyl ammonium Chlorochromate¹⁵, Quinoxalinium bromochromate¹⁶, Quinolinium bromo -chromate¹⁷, Pyridinium bromochromate¹⁸, Tetrabutylammonium tribromide¹⁹ 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-bromosuccinimide²⁰, N-bromosaccharin²¹, N-bromoacetamide²² and Chloramine-T²³ as oxidants have been reported. N-Chlorosuccinimide (NCS) is potential oxidizing agent²⁴⁻²⁵ and it seems that there are no reports about the kinetics of oxidation of benzhydrol by N-Chlorosuccinimide (NCS). The present work reports kinetics and mechanism of PTA catalyzed oxidation of benzhydrol by N-Chlorosuccinimide (NCS) in 30 % acetic acid.

Experimental Materials

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

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. Furthermore, the double reciprocal plots of k^{-1} versus $[\text{substrate}]^{-1}$ are linear with positive intercept on Y-axis (Fig. II). These results lead the following conclusions:

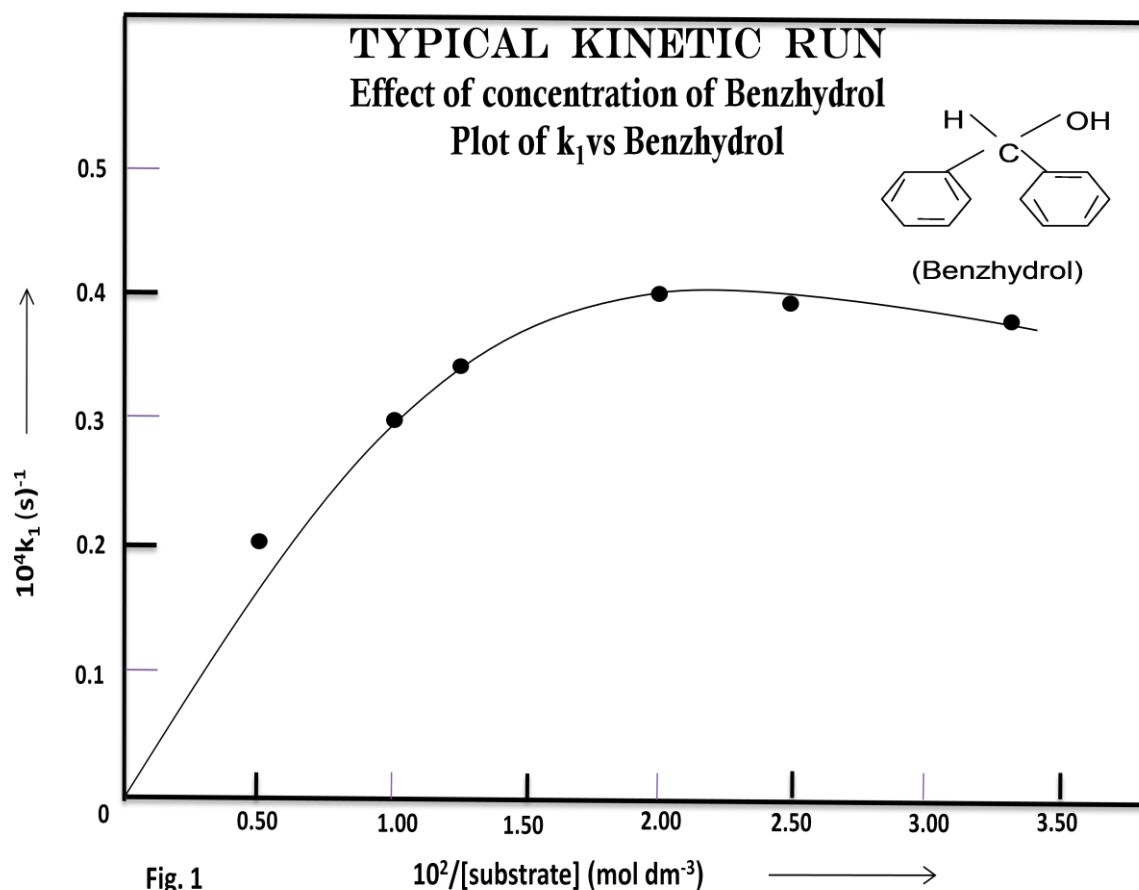
- (a) The order with respect to all the benzhydrol varies from one to zero showing fraction order.
- (b) There is kinetic evidence for the rigid intermediate complex formation between oxidant and benzhydrol in a pre-equilibrium step at transition state.

Table : I

Dependence of rate on the variation of the concentration of benzhydrol

[NCS]	=	$2.50 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$;
[PTA]	=	$3.33 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$;
HOAc-H ₂ O	=	30% (v/v) ;
Temp.	=	303 ⁰ K

SN	$10^2 \times$ [Benzhydrol] (mol dm ⁻³)	10^4 k_1 (s ⁻¹)	$10^{-2}/$ [Benzhydrol] (mol dm ⁻³)	$\frac{10^{-4}}{k_1}$	$100 k_2 = \frac{k_1}{[\text{Benzhydrol}]}$ (mol ⁻¹ s ⁻¹)
1.	0.50	1.13	2.00	0.884	2.26
2.	1.00	2.00	1.00	0.500	2.09
3.	1.25	2.32	0.80	0.431	1.85
4.	2.00	3.43	0.50	0.291	1.71
5.	2.50	3.56	0.40	0.297	1.34
6.	3.33	3.15	0.30	0.317	0.93

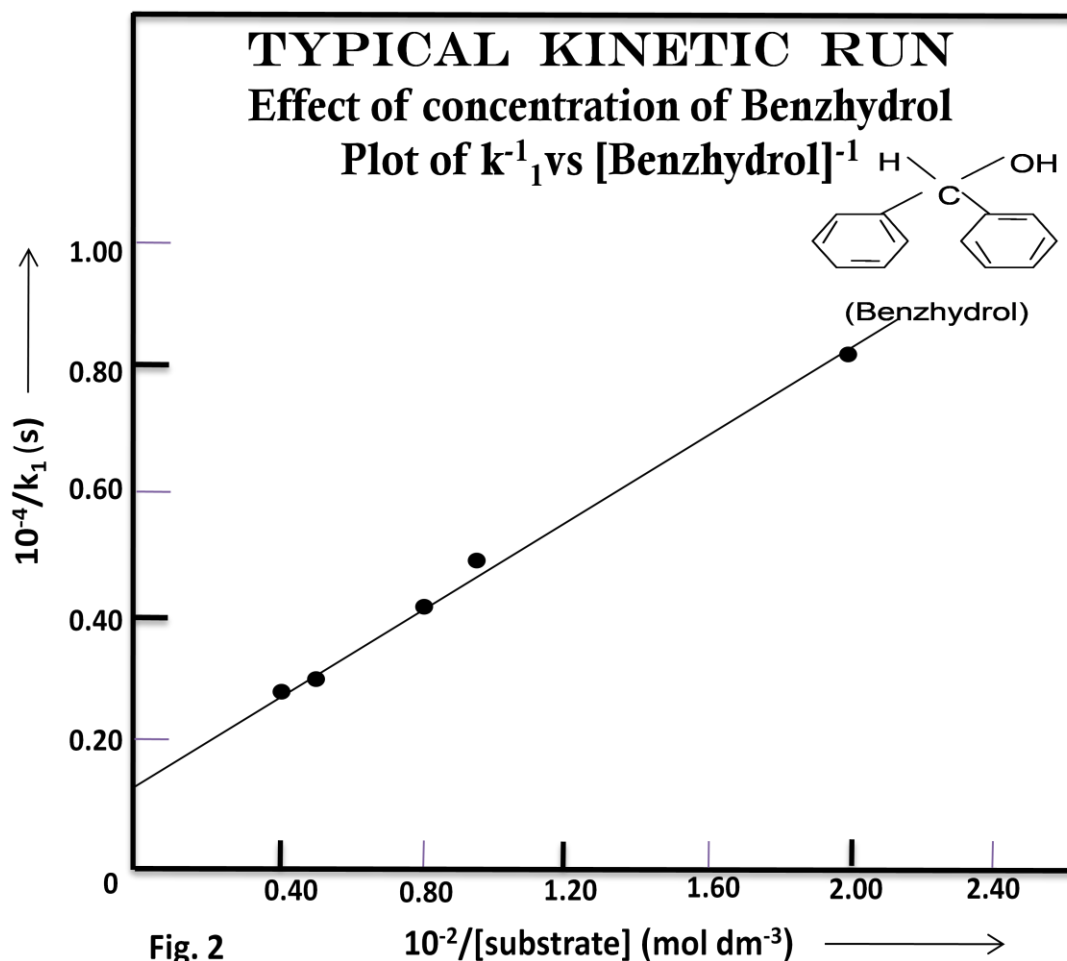


[NCS] = $2.50 \cdot 10^{-3} \times$ (mol dm⁻³);

[PTA] = $3.3310^{-4} \times$ (mol dm⁻³);

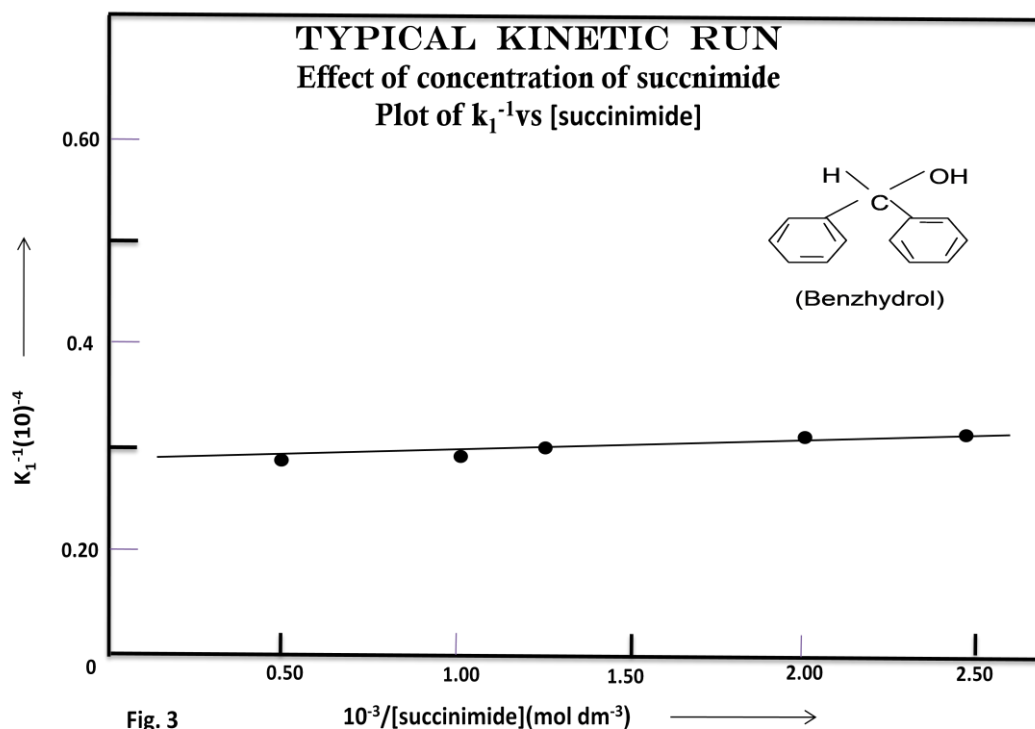
HO-Ac-H₂O = 30 % (v/v);

Temp. = 303 ° K



[NCS] = $2.50 \cdot 10^{-3} \times (\text{mol dm}^{-3})$;
[PTA] = $3.33 \cdot 10^{-4} \times (\text{mol dm}^{-3})$;
HO-Ac-H₂O = 30% (v/v);
Temp. = 303 ° K

Similar complex kinetic has also been reported by oxidation of above substrate with NBP²⁶. 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].



[NCS] = 2.50×10^{-3} (mol dm⁻³);
 [Substrate] = 2.00×10^{-2} (mol dm⁻³);
 [PTA] = 3.33×10^{-4} (mol dm⁻³);
 HO-Ac-H₂O = 30% (v/v);
 Temp. = 303 ° K

Table : 2

Dependence of rate on the concentration of reactant product succinimide

[NCS] = 2.50×10^{-3} (mol dm⁻³);
 [Substrate] = 2.00×10^{-2} (mol dm⁻³);
 [PTA] = 3.33×10^{-4} (mol dm⁻³);
 HOAc-H₂O = 30% (v/v);
 Temp. = 303⁰K

S.N.	[Succinimide] $\times 10^3$ (mol dm ⁻³)	Benzhydrol $10^4 k_1$ (s ⁻¹)
1.	0.00	3.43
2.	0.50	3.41
3.	1.00	3.39
4.	1.25	3.31
5.	2.00	3.28

6.	2.50	3.22
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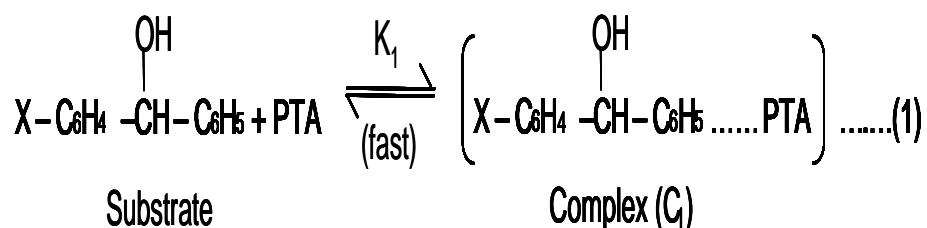
The negligible salt effect shows that the rate determining step involves either neutral species or an ion and a neutral molecule.^{27,28} Hence the effect of concentration of succinimide on the oxidation of benzhydrol was studied by adding varying concentration of succinimide. From Table: 2. It is evident that with increasing concentration of added succinimide, the rate of oxidation of benzhydrol decreases. The plot of k^{-1} Vs. [succinimide] is obtained linear for benzhydrol.(Fig. -3)

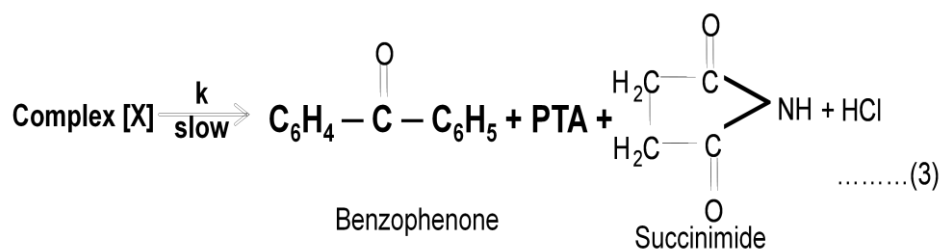
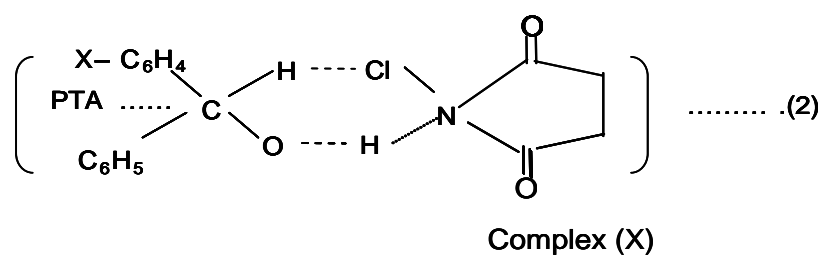
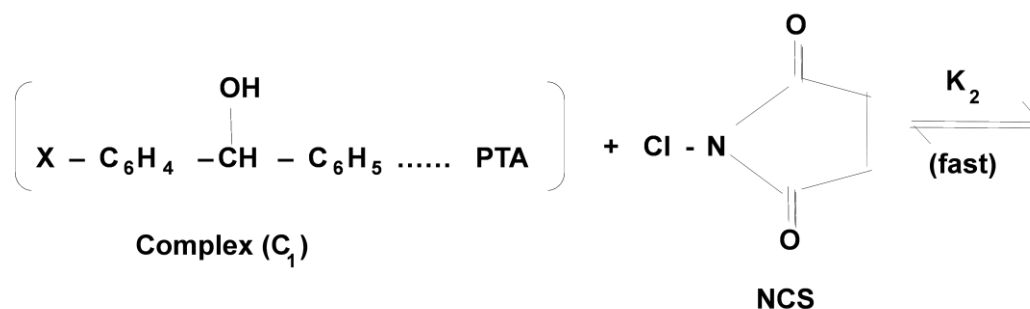
It has been observed that addition of little amounts of Cu^{2+} accelerates the reaction rate in all the cases while added Mn^{2+} ions have been found to retard the oxidation rate.

There was no significant change in rate constant was observed with variation of H^+ ion. It was found that the ionic strength of the reaction medium has negligible effect on the reaction rate²⁹.

Variation of Phthalimide, one of the products of oxidation, had negligible effect on the rate of reaction. The oxidation reactions of benzhydrol with N-Chlorosuccinimide (NCS) 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 = H₃PW₁₂O₄₀ (Phosphotungstic acid)

NCS = N-chlorosuccinimide

X = Benzhydrol.

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.

Acknowledgements

The authors are thankful to the principal S.G.S. Govt. Auto. P.G. College, Sidhi (M.P.) for providing laboratory facilities.

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