Kinetics of Oxidation of Acetyl &Benzoyl acetone by N-Chlorosaccharinin Acetic Acid-Water Medium

SushilKumar[1], Siddharth Singh[1]and R.P. S.Chauhan[1,*]
[1](PG Department of Chemistry, Magadh University, Bodh Gaya, Bihar 824234)

Abstract: *The current study shows that the detailed kinetics of the oxidation of the acetyl acetone and benzoyl acetone experiments were obtained initially by N–Chlorosaccharin in acetic acid and water medium to obtain the conditions when the reaction rate is quantitatively measurable and the observed reaction proceeds very smoothly to proceed for completion. The effect of the initial concentration of N–Chlorosaccharin, effect of the variation of initial concentration of the substrate in the reaction, effect of the concentration of per chloric acid present in the reaction, effect of the temperature on the rate of the reaction and ffect of dielectric constant of the medium has been studied.*

Background*: Oswal and Pathak studied the kinetics of the reaction and mechanism of the oxidation of benzoyl acetone by using manganic pyrophosphate in water acetic acid mixture. The order of reaction for both Mn(III) and diethyl malonate are one. oxidation of benzoyl acetone and acetyl acetone2 and other carbonyl compounds by hexacyano ferrate (III) exhibits Ist order dependence in oxidant, substrate and alkali. Oxidation of acetyl acetone18 studied with peroxomono phosphoric acid and H2O2 at PH 8–13.7.*

Materials and Methods*: Preparation of solutions and its standardization has been performed as follows. The NCSA of higher purity (>99%) in good yield (90%) was obtained by passing a very slow stream of chlorine gas through suspension of saccharin in water and simultaneous adding of sodium bicarbonate (s) in small installments for the neutralization the HCl produced.*

Results*: The plots of k1 vs. [diketones] are linear and it pass through the origin. Further the plot bend towards x-axis which present that the order for diketones and esters varies from 1 to 0. The double reciprocal plots obtained between 1/k1 vs. 1/[diketones] or 1/[esters] are linear and the plot show the positive intercept on the y-axis suggesting the formation of complex between oxidant and substrate species.*

Conclusion:*The current study shows that the detailed kinetics of the oxidation of the acetyl acetone and benzoyl acetone experiments were obtained initially by N–Chlorosaccharin in acetic acid and water medium to obtain the conditions when the reaction rate is quantitatively measurable and the observed reaction proceeds very smoothly to proceed for completion. The effect of the initial concentration of N–Chlorosaccharin, effect of the variation of initial concentration of the substrate in the reaction, effect of the concentration of per chloric acid present in the reaction, effect of the temperature on the rate of the reaction and ffect of dielectric constant of the medium has been studied.*

Key Word*: Kinetics, Oxidation, Acetone, Ester,N-Chlorosaccharin, Acetic Acid*

I. Introduction

Oswal and Pathak[1] studied the kinetics of the reaction and mechanism of the oxidationof benzoyl acetone by using manganic pyrophosphate in water acetic acid mixture. The order of reaction for both Mn(III) and diethyl malonate are one. oxidation of benzoyl acetone and acetyl acetone[2] and other carbonyl compounds by hexacyano ferrate (III) exhibits I[st] order dependence in oxidant, substrate and alkali. Oxidation of acetyl acetone[18] studied with peroxomono phosphoric acid and H_2O_2 at PH 8–13.7. The mechanism of above reaction was given as nucleophilic attach of peroxo species on both diketo and enol forms of the substrate followed by 0–0 bond fission has been postulated.The study of oxidation of dimethyl malonate in presence and absence of Mn^{+2} ions at constant ionic strength was made by Oswal S.L.[21] uncatalysed oxidation depends on total [Cr(VI)] and catalyzed on fraction of $[H\ CrO_4^-]$. Michaelis–menten type dependence of rate on [ester] rules out direct single step three electron oxidation structure of complex is as follow. In catalyzed oxidation Mn(II) forms 1:1 chelate complex with the enol with the enol which is oxidized by $[H\ CrO_4^-]$ to Mn(III) complex. This complex decomposes by a slow one electron inner-sphere transition to give fee radical. The oxidation of Pentane 2, 4–dione by chromium (III) in aqueous solution studied by Hynes[22] et al. This studied made 55[O]C. The kinetics are consistent with a mechanism in which $[Cr(H_2^O)_6]^{3+}$ and $[Cr(H_2^O)_5(OH)]^{2+}$ react with the enol forms.

The first kinetic exploration with N–Chlorosaccharin was carried out by Sundaram et al.[37]It was reported the acid catalysed oxidation process of benzoyl alcohol along with its substituted derivatives by NCSA in water acetic acid mixture in presence of added saccharin. These reactions exhibit first order dependence in alcohol NCSA and [H+].On the basis of saccharin and acid effect, they proposed HOCI as an active oxidant species. The kinetic results suggest a rate determining direct oxidation of alcohol with C–H fission.Oxidation of

hydroxyl acids by NCSA. In 1991 Khan et al.[38] examined kinetics feature of oxidation of process of and benzylic acid oxidandelic acid by N–Chlorosaccharin in under the aqueous acetic acid medium. The rate of reaction with respect to substrate and NCSH was reported to be first order and the $HClO_4$ acid has been found to have retarding effect. The dielectric constant of medium has shown decreasing trend.These co-workers have also been reported HOCl as an active oxidant species. On the basis of kinetic data, the suggested mechanism. One carbonyl and one ester group is present in acetoacetic ester whereas two ester groups present in case of di ethyl malonate (malonic ester). These methylene group is commonly known as active methylene moiety.

The acetyl acetone is an acetyl derivative of acetone and formulated as $CH_3–Co–CH_2–CO–CO_3$. It is an diketone. Its IUPAC name is 2,4 pentane dione. The compound is mobile colourless liquid. Its boiling point at 139^OC. The compound is simple it is in water sparingly (soluble in 8 volume cold water). It is readily dissolve in organic solvent. The keto-enol tautomerism occurs in such compound.The enol content in acetyl acetone is about 80 it was reported.[39,40]The benzoyl acetone is a benzoyl derivative of acetone. It is formulated as $CH_3–CO–CH_2–CO–CO_6–H_5$. It is also a di ketone and its. IUPAC name is 1–phenyl 1,3, butane dione, which a crystalline solid, colourless having melting point of 61^OC. The compound is insoluble in water, at the same time it dissolve in organic solvents. The keto–enol. Tautomerism exhibits by this compound in dynamic equilibrium as below given.The third compound is ethyl aceto acetate or ethyl aceto ester, which is a ethyl ester of aceto acetic acid IUPAC name of this catalyzed is 3–keto butanoate. The compound is regarded as acetyl derivative of ethyl acetate. It has pleasant smell, with colourless liquid, it consists boiling point of about $180–181^OC$ The compound is sparingly soluble in water but interesting the compound dissolves readily in organic solvents.

The keto–enol tautomerism is take place in this compound also. The dynamic equilibrium of the both forms. In above compound the enol content is only 8% and keto content is 92%. This composition was found to vary with temperature and solvent, it is reported[39,40]. The enol form of diketone and keto–ester are to be stabilised by internal hydrogen bonding which is unavailable to keto form. The keto and enol form of acetoacetic ester have been isolated[41]. The enol form is a liquid even at $–78^OC$. and keto form melts at $–39^OC$. Each of them (keto or enol form) can be kept at room temperature for days in absence of acids or bases. The fourth compound is malonic ester, or di ethyl malonate.The diethyl malonate unlike aceto acetic ester exists in the keto form. It does not produce any colour with $FeCl_3$. It does not react with bromine. This lack of enolisability has been attributed to the weaker activating influence of the ester grouping. The malonic ester is a colourless liquid with a fruity pleasant smell. It boils at 199^OC. It is insoluble in water but soluble in organic solvents respectively.

II. Material and Methods

Preparation of solutions and its standardization has been performed as follows. The NCSA of higher purity (>99%) in good yield (90%) was obtained by passing a very slow stream of chlorine gas through suspension of saccharin in water and simultaneous adding of sodium bicarbonate (s) in small installments for the neutralization the HCl produced. Thebenzoyacetone was used of Emerck grade whereas the malonic ester was used of VEB grade. The precipitated NCSA was filtered off and the process of passing chlorine gas into the filtrate and filtering off the precipitate was repeated till no more precipitate was obtained. The NCSA is recrystallized by carbontetrachloride–hexane. Now the solution of NCSA so obtained was prepared by dissolving its weighed amount in 100% acetic acid of BDH grade and this solution kept in either amber colored flask or black paper were wrapped around it in a conical flask then addition 10ml of 2% potassium iodide solution was followed by 5ml of $4NH_2SO_4$. The liberation of iodine was titrated against standard solution of sodium thiosulphate using starch solution as an indicator.

III. Result and Discussion

The plots of k1 vs. [diketones] or [esters] are linear and it pass through the origin. Further the plot bend towards x-axis which present that the order for diketones and esters varies from 1 to 0. The double reciprocal plots obtained between 1/k1 vs. 1/[diketones] or 1/[esters] are linear and the plot show the positive intercept on the y-axis. suggesting the formation of complex between oxidant and substrate species.

Effect of perchloric acid on the reaction rate is also studied. The data obtained from kinetics studies have been collected for five folds change of per chloric acid at a certain concentration of other reactants. The results of the above variations are reported for aetyl acetone and benzoyl acetone. The result shows that the reaction velocity changes with the increase in the concentration of perchloric acid. The plots of k1 versus [HClO4] are linear passing through the origin and bends towards x–axis clearly indicating that, order with respect to acid for both the diketones and esters varies from 1 to 0. Though the reactions are acid catalyzed but the curve attains a limiting value at higher concentration of per chloric acid. The value of k2=k1/ [HClO4] are not constant for both the diketones and esters.

The slope value is varied at different part of the curve. At low concentration the slope value is one and slope value is less than one at higher concentration of perchloric acid it is again indicating that, both the

reactions are acid catalyzed and order with respect to acid is one to zero for both the diketones and esters respectively. Kolthoff5 et.al., reported that HClO4 acid catalyses the reaction rate as it has a relatively of greater strength than sulphuric acid in acetic and medium. Enol is involved in the rate determining step.
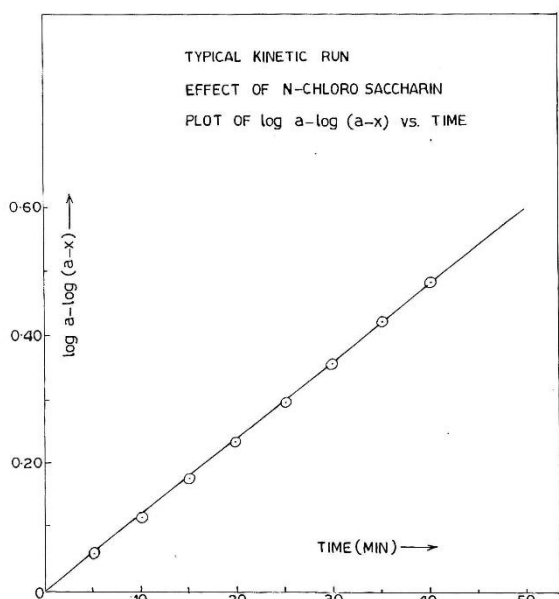

Fig-1a $[ACETYL\ ACETONE] = 2.50 \times 10^2 M$, HOAc – H₂O = 40% (V/V), $[NCSA] = 2.50 \times 10^3 M$, TEMP. = 40°C.
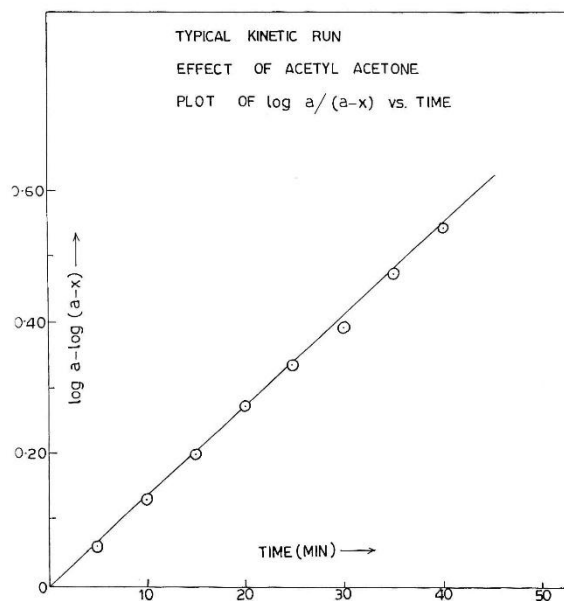
Fig.-1b $[ACETYL\ ACETONE] = 4.0 \times 10^2 M$, $[NCSA] = 2.50 \times 10^3 M$, HOAc-H₂O = 40% (V/V), TEMP. = 40°C.
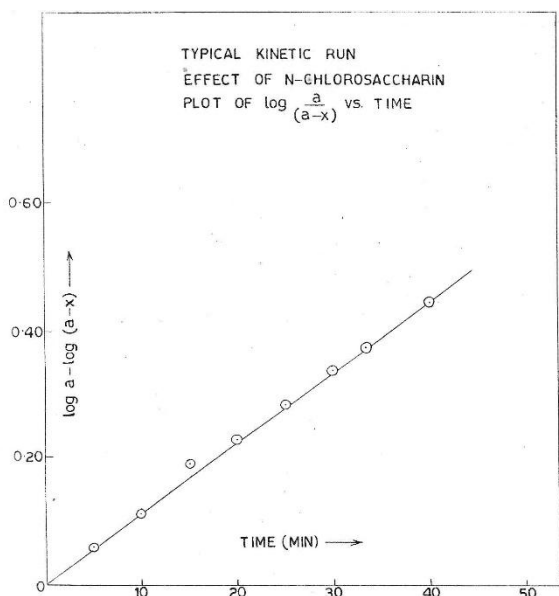
Fig.-2a $[BENZOYL\ ACETONE] = 2.50 \times 10^2 M$, $[NCSA] = 2.50 \times 10^3 M$, HOAc –H₂O = 70% (V/V), TEMP. = 55°C.
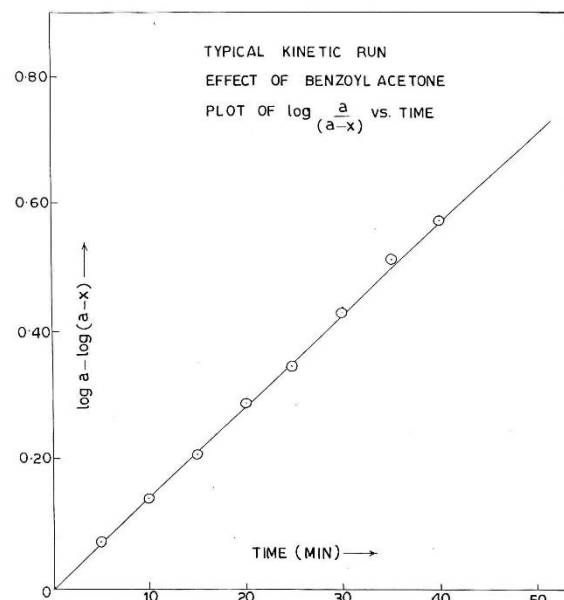
Fig.-2b $[BENZOYL\ ACETONE] = 4.0 \times 10^2 M$, $[NCSA] = 2.50 \times 10^3 M$, HOAc-H₂O = 70% (V/V), TEMP. = 55°C.

The above data reveal that first order rate constant increase with the increase in concentration of substrate. The value of rate constant. however, decreases with increase in concentration of diketones. Interestingly, the plot of k1 vs [AA] or [BA] is linear and pass through the origin. The plot shows the bend towards x-axis. It shows that the order in both the diketones varies between one and zero. The double reciprocal plots between 1/k1 vs 1/[AA] or 1/[BA] are linear having the positive intercept on y–axis suggesting the formation of complex between oxidant and both the diketones. The induction period decreases with increase in concentration of diketones. The reaction rate change is observed by change of the concentration of per chloric acid was measured by varying the concentration of perchloric acid when the concentration of the substrate,

present in the reaction, oxidant and composition of acetic acid-water was kept constant. The kinetic studied were made at their respective fixed temperature. A series of experiments were performed with acetyl acetone, benzoyl acetone and the results obtained for the effect of variation of NCSA on the reaction rate for its fivefold variation are reported. A close examination of the third and fourth columns of the aforesaid shows the first order kinetics with respect of oxidant. The plots of log (a-x) vs. time are straight lines, passing through origin indicating that the reaction under investigation follow first order kinetic with respect to oxidant.

According to Santappa3 et. al., oxidation of methyl ethyl ketone and cyclopentanone exhibits first order dependence on [TI III] and 3–Pentanone4–TI (III) oxidation obeys kinetic equation of pseudo first order. Dependence of rate on substrate is also depicted here. The next series of the experiments were carried out with diketones (acetyl acetone, benzoyl acetone). In the second series of the experiments the kinetic data have been collected with esters with a wide range of substrate concentrations (fivefold) are recorded, respectively. It means the rate constant increases with increase of the substrate. However, the value of 2nd order rate constant does not produce the similar result.

IV. Conclusion

The current study shows that the detailed kinetics of the oxidation of the acetyl acetone and benzoyl acetone experiments were obtained initially by N–Chlorosaccharin in acetic acid and water medium to obtain the conditions when the reaction rate is quantitatively measurable and the observed reaction proceeds very smoothly to proceed for completion. The effect of the initial concentration of N–Chlorosaccharin, effect of the variation of initial concentration of the substrate in the reaction, effect of the concentration of per chloric acid present in the reaction, effect of the temperature on the rate of the reaction and ffect of dielectric constant of the medium has been studied.

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