

Chemical Studies of Acetones and Esters using N-Chlorosaccharin in Acetic Acid-Water Medium

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Abstract: The current study shows that Steric hindrance may cause retarding (slower) rate of oxidation. AA exhibit the capacity of formation of chelate-ring, but due to be $-O-C_2H_5$ group more electrons are released in comparison to methyl group of AA and therefore the amount of the enol content is decreased. the rate of oxidation of benzoyl acetone is found to be slower, than that of acetyl acetone while benzoylacetone has higher enolic content rather than acetylacetone. This fact may be explained by the extra stability of formation of chelate-ring with intramolecular hydrogen bonding of enol of acetyl acetone, conjugate effect, resonance and steric hindrance. A perusal of the proceeding result confirms that the activity of N-Chlorosaccharin is very much limited. This is due to the restricted activity on ketones and esters in ordinary medium of solvent. At the same time, it is also concluded that the presence of acid does increase the activity at relatively higher temperature. Even then this study certainly a worthy contribution to the field of chemical kinetics by opening a new field with NCSA.

Background: Chemical kinetics is the study of reaction rates, the changes in the concentrations of reactants and products with time. The Mechanism of the reaction Acetoacetic ester with N-chlorosaccharin reagent in acetic acid water medium has been a vital problem to study and is in focus from last two decades. It has also been highlighted by German Chemist Ludwig-Ferdinand Wilhelmy from his work Chlorosaccharin (NCSA) was first prepared by chlorination of saccharin. 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 HOCl as an active oxidant species. The kinetic results suggest a rate determining direct oxidation of alcohol with C-H fission.

Materials and Methods: The ethyl aceto acetate 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.

Results: The typical runs for the several aspects of kinetic studies are carried out and following effects were studied. Effect of the initial concentration of N-Chlorosaccharin. Effect of the variation of initial concentration of the substrate in the reaction. Effect of dielectric constant of the medium, effect of saccharin on the rate of the reaction, effect of neutral salt on the reaction were studied. Effect of the concentration of per chloric acid present in the reaction and Effect of the temperature on the rate of the reaction are also studied.

Conclusion: The current study shows that Steric hindrance may cause retarding (slower) rate of oxidation. AA exhibit the capacity of formation of chelate-ring, but due to be $-O-C_2H_5$ group more electrons are released in comparison to methyl group of AA and therefore the amount of the enol content is decreased. the rate of oxidation of benzoyl acetone is found to be slower, than that of acetyl acetone while benzoylacetone has higher enolic content rather than acetylacetone. This fact may be explained by the extra stability of formation of chelate-ring with intramolecular hydrogen bonding of enol of acetyl acetone, conjugate effect, resonance and steric hindrance. A perusal of the proceeding result confirms that the activity of N-Chlorosaccharin is very much limited. This is due to the restricted activity on ketones and esters in ordinary medium of solvent. At the same time, it is also concluded that the presence of acid does increase the activity at relatively higher temperature. Even then this study certainly a worthy contribution to the field of chemical kinetics by opening a new field with NCSA.

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

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I. Introduction

Chemical kinetics is the study of the changes in the concentrations of reactants as well as reaction rates. The kinetics of oxidation of diphenyl methane using chromic acid in glacial acetic acid has been studied by stack and waters on the oxidation of chromic acid. It is found that the rate of reaction oxidation was rapid initially, further slackten and diphenyl methane present in the solution. It was observed that chromic cations $[Cr(II)]$ partially stop the reaction. It was found that the oxidation takes rapidly and finishes even at room temperature on addition of 2.5% of sulphuric acid. Benzophenone was found as product of oxidation and Benzhydrol or its acetic was no isolated finally.

Radha Krishnamurthi and Sushila Devi studied the kinetics of oxidation of ketones, i.e., benzoyl actions, ethylacetoacetate and actions by hexacyanoferrate (in) is aqueous ethanol. Oswal and Pathak¹¹ studied the kinetics of the reaction and mechanism of the oxidation of diethyl malonate by using manganic pyrophosphate in water acetic acid mixture. The order of reaction for both Mn(III) and diethyl malonate is one. oxidation of benzoyl acetone and acetoacetic ester¹⁶ and other carbonyl compounds by hexacyano ferrate (III) exhibits 1st order dependence in oxidant, substrate and alkali. Oxidation of acetyl acetone¹⁸ studied with peroxomono phosphoric acid and H₂O₂ at PH 8–13.7. The mechanism of above reaction was given as nucleophilic attack of peroxo species on both diketo and enol forms of the substrate followed by O–O 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 [HCrO₄⁻]. 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 [HCrO₄⁻] to Mn(III) complex. This complex decomposes by a slow one electron inner-sphere transition to give free radical. The oxidation of Pentane 2, 4–dione by chromium (III) in aqueous solution studied by Hynes²² et al. This studied made 55°C. The kinetics are consistent with a mechanism in which [Cr(H₂O)₆]³⁺ and [Cr(H₂O)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 HOCl 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 propanoic acid and benzilic 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 HClO₄ 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 aceto acetic 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 CH₃–CO–CH₂–CO–CO₃. It is an diketone. Its IUPAC name is 2,4 pentane dione. The compound is mobile colourless liquid. Its boiling point at 139°C. 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 CH₃–CO–CH₂–CO–CO₆–H₅. 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°C. 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°C 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 isolated⁴¹. The enol form is a liquid even at –78°C. and keto form melts at –39°C. 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 FeCl₃. 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°C. It is insoluble in water but soluble in organic solvents respectively.

II. Material and Methods

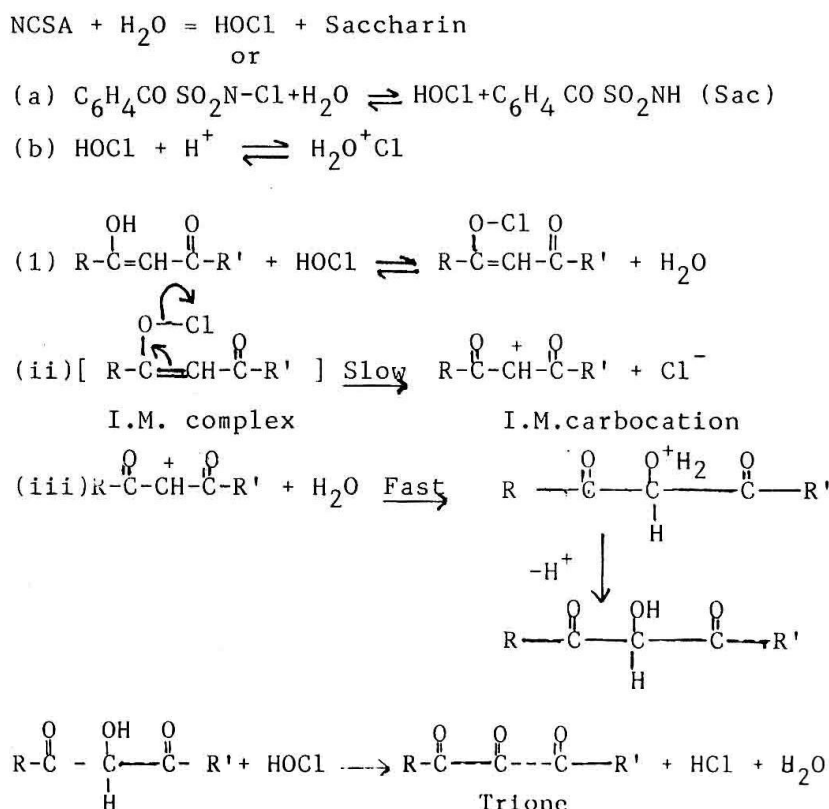
The ethyl aceto acetate was used of Emerck grade whereas the malonic ester was used of VEB grade. The precipitated NCSA was filtered off and the process of passing chlorine gas into the filtrate and filtering off the precipitate was repeated till no more precipitate was obtained. The NCSA is recrystallized 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 4NH₂SO₄. The liberation of iodine was titrated against standard solution of sodium thiosulphate using starch solution as an indicator. 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.

III. Result and Discussion

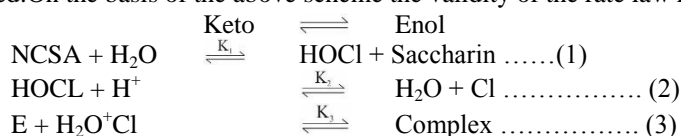
The typical runs for the several aspects of kinetic studies are carried out and following effects were studies. Effect of the initial concentration of N-Chlorosaccharin. Effect of the variation of initial concentration of the substrate in the reaction. Effect of dielectric constant of the medium, effect of saccharin on the rate of the reaction, effect of neutral salt on the reaction were studied. Effect of the concentration of per chloric acid present in the reaction and Effect of the temperature on the rate of the reaction are also studied.

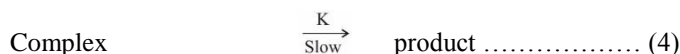
Mechanism of oxidation of diketones and esters are studied. The mechanism thus shows the intermediate complexes are formed by the attach of an electrophile. HOCl on esters and diketones during the rate determining step.



The presence of two carbonyl groups make the intermediate susceptible to oxidation by another equivalent of fresh HOCl which is consonance with the stoichiometric results. Enols are hydroxyl compounds, therefore such an alcohol attack of HOCl an enolic -OH may be reported.

The rearrangement in a series of fast steps to chloronium enolic ester (hypo chlorite intermediate) and finally the observed organic product. The plots of 1/k₁ versus 1/[diketones] or 1/[esters] give positive intercept on y-axis suggesting/exp. that intermediate formed are unstable.³³ The results obtained from kinetics shows that enolisation of esters is not rate determining step. Enol form of the ester react with HOCl on enolic-OH to form a hypo chlorite intermediate in the equilibrium. It finally goes through disproportionation /via in a number of fast steps and eventually the product has been obtained. The final products triketo ester on hydrolysis give us the corresponding acid, but the rate of hydrolysis of the ester has been found relatively negligible in comparison to that of oxidation of series of esters.³⁴ Hence hydrolytic reputure of ester linkage was suggested. On the basis of the above scheme the validity of the rate law may be confirmed by deriving it as





$$\text{Rate} = k [\text{complex}] \dots\dots\dots (5)$$

$$\text{Rate} = \frac{k K_1 K_2 K_3 [E] [NCSA] [H^+]}{[S]} \dots\dots\dots (6)$$

Applying steady state hypothesis

$$[NCSA]_T = [NCSA] + [HOCl] + H_2O^+ Cl + [Complex] \dots (7)$$

Substituting the value of [NCSA] by [NCSA]_T

$$\text{Rate} = \frac{K_1 K_2 K_3 k [E] [H^+] [NCSA]_T}{[S] + K_1 + K_2 + K_3 [H^+] + K_1 K_2 K_3 [E] + [H^+]} \dots (8)$$

$$k_{\text{obs}} = \frac{\text{Rate}}{[NCSA]_T} = \frac{K_1 K_2 K_3 k [E] [H^+]}{[S] + K_1 + K_2 + K_3 [H^+] + K_1 K_2 K_3 [E] + [H^+]} \dots (9)$$

At very low concentration H⁺ assuming when K₁K₂ is quite small than K₃ i.e. (K₁K₂ < K₃) then [S] + K₁ + K₂ < K₁K₂ < K₃ [H⁺] + K₁K₂K₃ [E] [H⁺]

Under such a condition the rate equation (9) reduces to

$$k_{\text{obs}} = k$$

The rate law accounts for the first order kinetics and explains all the experimental facts. Structure and reactivity have been discussed here. In present investigation on the basis of kinetic features observation, the order of reactivity in following sequence. Acetylacetone > benzoylacetone > ethyl acetoacetate > malonic ester

The rate of oxidation of benzoyl acetone is found to be slower, than that of acetyl acetone while benzoylacetone has higher enolic content rather than acetylacetone. This fact may be explained by the extra stability of formation of chelate-ring with intramolecular hydrogen bonding of enol of acetyl acetone, conjugate effect, resonance and steric hindrance.

Steric hindrance may cause retarding (slower) rate of oxidation. EAA exhibit the capacity of formation of chelate-ring, but due to be -O-C₂H₅ group more electrons are released in comparison to methyl group of AA and therefore the amount of the enol content is decreased.

The lowest enol content in diethyl malonate is due to the presence of two ethyl group. The hindrance is majorly observed in diethyl malonate. It is reported by Newman's rule³⁶ of six the ester group, hinders the rate of oxidation and obeying above order of reactivity. Similar views reported chromic acid oxidation of ethyl lactate³⁷ and diethyl malonic acid oxidation by Ce (IV) Bakore³⁸ et.al. Reported that introduction of ester group in Place of -COOH, retards the rate of oxidation. It appears from the summing up of above experimental results that, the steric hinderance of ester group in the formation of complex which slow down the reaction velocity dueto reduction (disproportionation) of complex concentration. The slow rate of oxidation may be explained by the less electron with drawing effect of -COOCH₃ group than -COOH group.

Michail-Menion's plot did not give intercept indicating that intermediate formed is not stable³⁵. A very useful information regarding the mechanistic route of reaction can be obtained by activation parameters. The values of different thermodynamic parameters for NCSA oxidation of active methylene compounds may be summarised as

Substrate	Ea KJ mole ⁻¹	A Sec ⁻¹	ΔH [*] KJ mole ⁻¹	ΔG [*] KJ mole ⁻¹	-ΔS [*] JK mole ⁻¹
Acetyl acetone	27.67 +0.375	3.75x10 ⁻¹⁵ +0.5771x10 ⁻¹⁵	26.84 +0.2606	87.92 +0.2915	47.33 +0.0384
Benzoyl acetone	41.82 +0.1298	1.809x10 ⁻⁷ +0.1188x10 ⁻⁷	36.82 +0.5671	93.30 +0.4256	40.35 +0.2432
Ethyl aceto acetate	48.61 +0.303	3.12x10 ⁻³ +0.0669x10 ⁻³	47.42 +0.2808	89.38 +0.2815	31.44 +0.1143
Malonic ester	49.25 +0.11809	3.36x10 ⁻³ +0.0885x10 ⁻³	48.27 +0.3580	93.35 +0.2141	33.28 +0.06664

The perusal of the above table clearly furnish evidence that the value of activation energy (E_a) is lowest for the fastest reaction and vice-versa, i.e. E_a is between 27.67 to 49.25 KJ mole⁻¹ specifically indicating that reaction is enthalpy controlled.

IV. Conclusion

The current study shows that Steric hindrance may cause retarding (slower) rate of oxidation. AA exhibit the capacity of formation of chelate-ring, but due to be $-O-C_2H_5$ group more electrons are released in comparison to methyl group of AA and therefore the amount of the enol content is decreased. The rate of oxidation of benzoyl acetone is found to be slower, than that of acetyl acetone while benzoylacetone has higher enolic content rather than acetylacetone. This fact may be explained by the extra stability of formation of chelate-ring with intramolecular hydrogen bonding of enol of acetyl acetone, conjugate effect, resonance and steric hindrance. A perusal of the proceeding result confirms that the activity of N-Chlorosaccharin is very much limited. This is due to the restricted activity on ketones and esters in ordinary medium of solvent. At the same time, it is also concluded that the presence of acid does increase the activity at relatively higher temperature. Even then this study certainly a worthy contribution to the field of chemical kinetics by opening a new field with NCSA.

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