

Quantitative determination of Malonic ester with N-chlorosaccharin reagent in acetic acid water medium: Mechanism and Kinetics Study

Sushil Kumar¹ and R.P. S. Chauhan^{1,*}

¹(PG Department of Chemistry, Magadh University, Bodh Gaya, Bihar 824234)

Abstract: The present study describes the kinetics study of Malonic ester with N-chlorosaccharin reagent in acetic acid water medium through kinetic study. The result confirms that the activity of N-chlorosaccharin is limited and it is due to the restricted activity on ketones/esters in ordinary medium of solvent. Further it concluded that the presence of acid does increase the activity at relatively higher temperature. Therefore, this study worth contribution in the field of chemical kinetics by opening a new field with NCSA.

Background: Chemical kinetics describes the time evolution of a well-stirred chemically reacting system in a way that takes into account the fact that molecules come in whole numbers and exhibit some degree of randomness in their dynamical behavior. It deals with the investigations of how different experimental conditions may produce an effect on the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. The Mechanism of the reaction Malonic 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.

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. 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.

Results: A detailed survey of the experimental results clearly show that, the oxidation of acetyl acetone at room temperature in acetic acid-water medium with NCSA is slightly fast, but can be measured while that of benzoyl acetone and both the esters proceed at a negligible speed and hence their oxidation was carried out at higher temperature. Typical kinetics runs representing the various aspects of the kinetic studies are carried out as follows: Effect of the initial concentration of N-Chlorosaccharin, effect of the variation of initial concentration of the substrate on the kinetic studies, effect of the concentration of per chloric acid on the kinetic studies, effect of temperature of the reaction rate, effect of dielectric constant of the medium on the kinetic studies, effect of saccharin on the rate and effect of neutral salt on the Kinetic studies have been monitored.

Conclusion: The current study gives a kinetics study for the quantitative determination of malonic ester with N-chlorosaccharin reagent in acetic acid water medium. The study reveals 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: Malonic ester, N-chlorosaccharin reagent, Acetic acid

Date of Submission: 20-09-2020

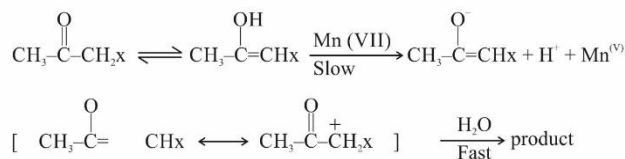
Date of Acceptance: 04-10-2020

I. Introduction

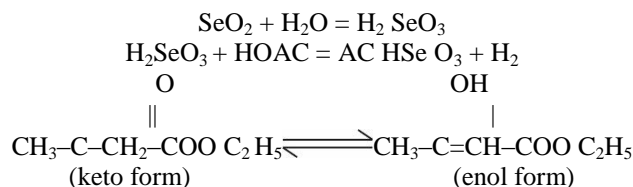
Chemical kinetics describes the time evolution of a well-stirred chemically reacting system in a way that takes into account the fact that molecules come in whole numbers and exhibit some degree of randomness in their dynamical behavior. It deals with the investigations of how different experimental conditions may produce an effect on the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction.

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.¹ It has also been highlighted by German Chemist Ludwig-Ferdinand Wilhelmy from his work.²The 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.

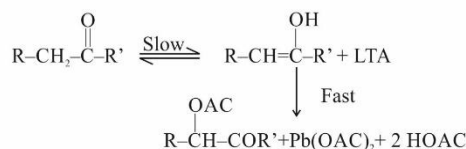
It is found that the rate of reaction oxidation was rapid initially, further slackten and diphenyl methane present in the solution. It was observed that chromic cations Cr(II) partially stops the reaction. It was found that the oxidation takes rapidly and finishes even at room temperature on addition of 2.5% of sulphuric acid. Benzophewene was found as product of oxidation and Benzhydrol or its acetic was not isolated finally. Radha Krishnamurthi and Sushila Devi studied the kinetics of oxidation of ketones, i.e., benzoyl acetone, ethylacetoacetate and acetone by hexacyanoferrate (in) in 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.

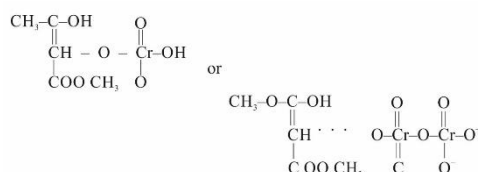


oxidation of benzoyl acetone and acetoacetic ester¹⁶ and other carbonyl compounds by hexacyano ferrate (III) exhibits 1st order dependence in oxidant, substrate and alkali.



Oxidation of acetyl acetone¹⁸ studied with peroxomonophosphoric acid and H₂O₂ at PH 8–13.7. The mechanism of above reaction was given as nucleophilic attack of peroxy 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 uncatalyzed 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.

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. 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 coloured 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 4N H₂SO₄. The liberation of iodine was titrated against standard solution of sodium thiosulphate using starch solution as an indicator.

For the kinetic study of oxidation of malonic ester, diketones and esters i.e. benzoyl acetone, malonic ester, acetyl acetone, by N–Chlorosaccharin. Series. The samples of acetyl acetone (K. light AR) and benzoyl acetone (Emerck) used in this kinetic study with standard grade. The malonic ester was used of Emerck grade

whereas the malonic ester was used of VEB grade. Other chemical such as acetic acid used BDH grade, potassium iodide is used of BDH grade. The sulphuric acid is used of BDH grade. The sodium thiosulphate (hypo) is used of (BDH) grade.

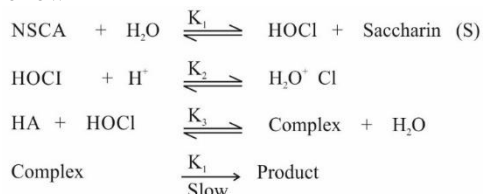
The following typical kinetics runs representing the various aspects of the kinetic studies are carried out as follows: Effect of the initial concentration of N-Chlorosaccharin, effect of the variation of initial concentration of the substrate on the kinetic studies, effect of the concentration of per chloric acid on the kinetic studies, effect of temperature of the reaction rate, effect of dielectric constant of the medium on the kinetic studies, effect of saccharin on the rate and effect of neutral salt on the Kinetic studies have been monitored.

III. Result and Discussion

A detailed survey of the experimental results clearly show that, the oxidation of acetyl acetone at room temperature in acetic acid-water medium with NCSA is slightly fast, but can be measured while that of benzoyl acetone and both the esters proceed at a negligible speed and hence their oxidation was carried out at higher temperature (BA – 55°C, EAA- 60°C and ME - 60°C).

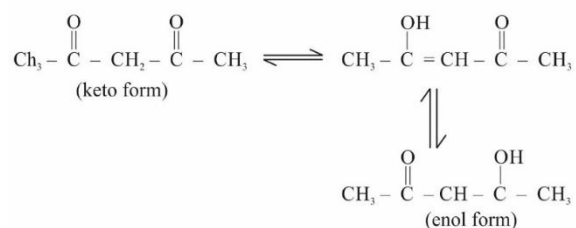
The first kinetic exploration with N-Chlorosaccharin was carried out by Sundaram et al.³⁷ It was reported the acid catalyzed oxidation process of benzoyl alcohol along with its substituted derivatives by NCSA in water acetic acid mixture in presence of added saccharin. These reactions exhibit first order 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 has been checked. In 1991 Khan et al.³⁸ examined kinetics feature of oxidation of process of andbenzylic 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 as follow

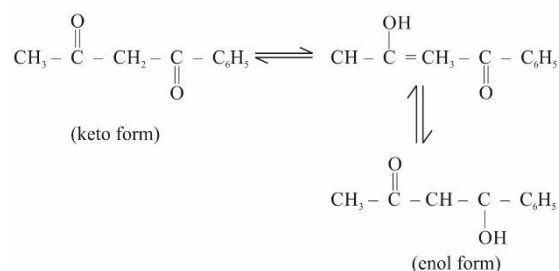


One carbonyl and one ester group are present in malonic ester whereas two ester groups present in case of di ethyl malonate (malonic ester). These methylene group is commonly known as active methylene moiety.

The acetyl acetone is an acetyl derivative of acetone. It is a 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 dissolved in organic solvent. The keto-enol tautomerism occurs in such compound.

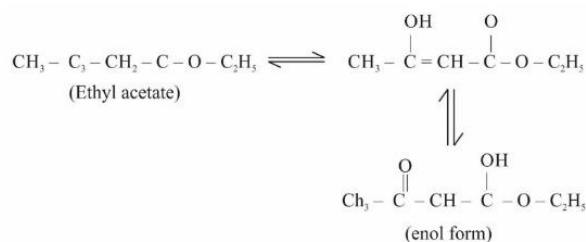


The enol content in acetyl acetone is about 80 it was reported.^{39,40} The benzoyl acetone is a benzoyl derivative of acetone. It is formulated as CH₃-CO-CH₂-CO-C₆H₅. It is also a di ketone and its IUPAC name is 1-phenyl 1,3, butane dione, which a crystalline solid, colourless having melting point of 61°C. The compound is insoluble in water, at the same time. It dissolves in organic solvents. The keto-enol. Tautomerism exhibits by this compound in dynamic equilibrium as below given.

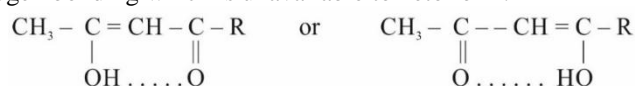


The third compound is ethyl acetoacetate ester, which is an ethyl ester of aceto acetic acid IUPAC name of this cataysed is 3-keto butanoate. The compound is regarded as acetyl derivative of ethyl acetate. It has pleasant smell, with colourless liquid, it consists boiling point of about 180–181°C. The 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 each form is given as below



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 is to be stabilized 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. It is di ethyl ester of malonic acid and formulated as

The diethyl malonate exists in the keto form. It does not produce any colour with FeCl₃. It does not react with bromine. This lack of formation of enol 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.

IV. Conclusion

The current study gives a kinetics study for the quantitative determination of malonic ester with N-chlorosaccharin reagent in acetic acid water medium. The study reveals 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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