

Kinetics of Oxidation of Acetyl and Benzoylacetone by N-Chlorosaccharin in Acetic Acid Water Medium

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Abstract: The current study shows that the rate of oxidation of benzoyl acetone (BA) is found to be slower, than that of acetyl acetone while benzoylacetone has higher enolic content rather than acetylacetone (AA). 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. It exhibits the capacity of formation of chelate-ring, but due to be $-O-C_2H_5$ group more electrons are released in competition to methyl group of AA and therefore the amount of the enol content is decreased.

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. N-Chlorosaccharin (NCSA) was first prepared by chlorination of saccharin.

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: The 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 k_1 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 $1/k_1$ 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.

Conclusion: The current study shows that 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. It exhibits 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.

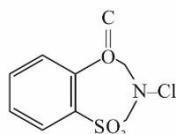
Key Word: Kinetics, Oxidation, Acetyl acetone, Benzoyl acetone, N-Chlorosaccharin, Acetic Acid

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I. Introduction

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.¹ It has also been highlighted by German Chemist Ludwig-Ferdinand Wilhelmy from his work.² N-Chlorosaccharin³³ (NCSA) was first prepared by chlorination of saccharin.



The $\begin{array}{c} | \\ -N-H \end{array}$ group of an imide is acidic to a much higher degree than in an amide. This is because of the fact that anion can be stabilized by resonance. The acyl and sulphonyl group provide a large orbital for electron³⁴ delocalization. Bachawat³⁵ et al. was reported that $>N-Cl$ bond under goes heterolytic fission in polar

medium producing chloronium ion (Cl^+), a stronger oxidant than bromonium ion (Br^+). He further observed that, NCSA can be advantageously used both as an oxidizing agent as well as chlorination for allylic and benzylic substances. The stoichiometrically ratio was found as 1:2 and 1:1. The yield of benzyl dehyde was reported 78 to 84%. The nature of product of these acids suggested the cleavage of C-C bond in the mechanistic step. Typical hydrocarbons eg. cyclohexene, 2-methyl cyclohexene, benzyl chloride, 2-chloro methyl benzene and O-nitro benzyl chloride. During the investigation, benzoyl peroxide was utilized as a source of free radical. The percentage yield of allylic chlorination product was reported to be 30-50. 3-chloro-cyclohexene was identified as the product of cyclohexene by Co-TLC and super imposable I.R. N-Chlorosaccharin was also employed for the chlorination of phenol³⁶.

Oxidation of alcohols by N-Chlorosaccharin is very first performed 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.

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 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

A detailed survey of the experimental results clearly shows 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 - $55^{\circ}C$). Typical kinetic runs. The typical runs for the several aspects of kinetic studies are carried out as: 1. Effect of the initial concentration of N-Chlorosaccharin. 2. Effect of the variation of initial concentration of the substrate in the reaction. 3. Effect of the concentration of per chloric acid present in the reaction. 4. Effect of the temperature on the rate of the reaction. 5. Effect of dielectric constant of the medium. 6. Effect of saccharin on the rate of the reaction. 7. Effect of neutral salt on the reaction. The detailed experimental data is as follows.

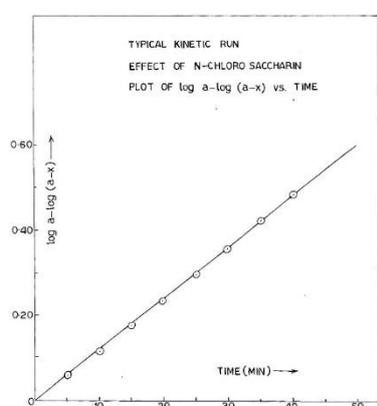


Fig-1a $[ACETYL\ ACETONE] = 2.50 \times 10^{-3} M$, $HOAc-H_2O = 40\% (V/V)$, $[NCSA] = 2.50 \times 10^{-3} M$, $TEMP = 40^{\circ}C$.

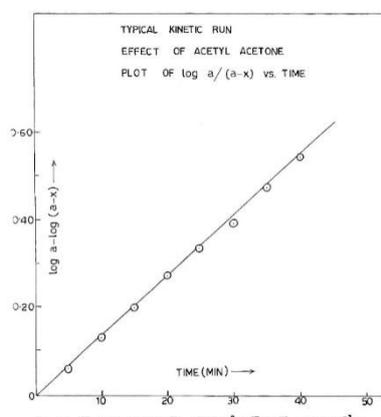


Fig-1b $[ACETYL\ ACETONE] = 4.0 \times 10^{-3} M$, $[NCSA] = 2.50 \times 10^{-3} M$, $HOAc-H_2O = 40\% (V/V)$, $TEMP = 40^{\circ}C$.

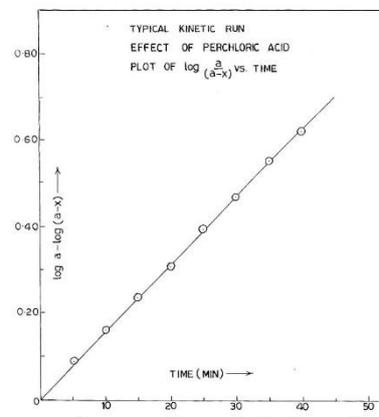


Fig-1c $[ACETYL\ ACETONE] = 2.50 \times 10^{-3} M$, $[NCSA] = 2.50 \times 10^{-3} M$, $HOAc-H_2O = 40\% (V/V)$, $[HClO_4] = 1.0 \times 10^{-2} M$, $TEMP = 40^{\circ}C$.

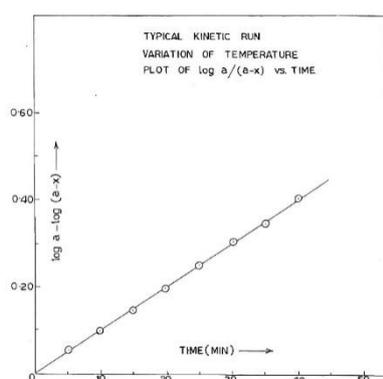


Fig-1d [ACETYL ACETONE] = 2.50×10^{-2} M, [NCSA] = 2.50×10^{-3} M, HOAc-H₂O = 40% (V/V), TEMP = 35°C.

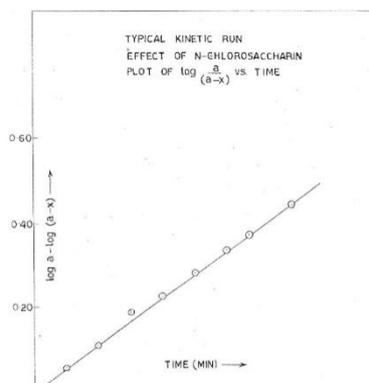


Fig-2a [BENZYL ACETONE] = 2.50×10^{-2} M, [NCSA] = 2.50×10^{-3} M, HOAc-H₂O = 70% (V/V), TEMP = 55°C.

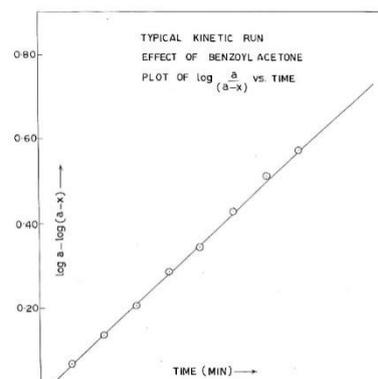


Fig-2b [BENZYL ACETONE] = 4.0×10^{-2} M, [NCSA] = 2.50×10^{-3} M, HOAc-H₂O = 70% (V/V), TEMP = 55°C.

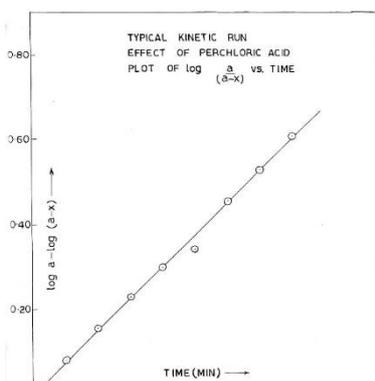


Fig-2c [BENZYL ACETONE] = 2.50×10^{-2} M, [NCSA] = 2.50×10^{-3} M, HOAc-H₂O = 70% (V/V), [HClO₄] = 2.0×10^{-2} M, TEMP = 55°C.

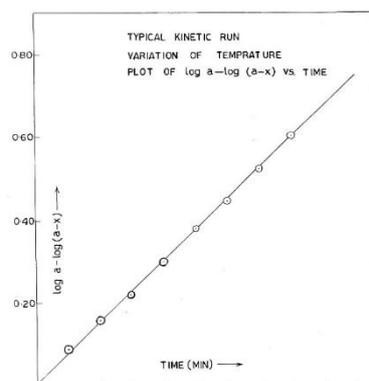


Fig-2d [BENZYL ACETONE] = 2.50×10^{-2} M, HOAc-H₂O = 70% (V/V), TEMP = 60°C, [NCSA] = 2.50×10^{-3} M.

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 k_1 vs [AA] or [BA] is linear and pass through the origin. The plot shows the bend towards x-axis (Fig. III 3 & 4) It shows that the order in both the diketones varies between one and zero. The double reciprocal plots between $1/k_1$ 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.

The plots of k_1 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 $1/k_1$ 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 acetyl acetone and benzoyl acetone. The result shows that the reaction velocity changes with the increase in the concentration of perchloric acid. The plots of k_1 versus $[\text{HClO}_4]$ 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 perchloric acid. The value of $k_2 = k_1 / [\text{HClO}_4]$ 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 HClO_4 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.

IV. Conclusion

The current study shows that 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. AA exhibit the capacity of formation of chelate-ring, but due to be $-\text{O}-\text{C}_2\text{H}_5$ group more electrons are released in comparison to methyl group of AA and therefore the amount of the enol content is decreased.

References

- [1]. Briody, J.M. and Moore, R.A.J. Chem. So., 1972. 179.
- [2]. Raghunath Rao, P. and Sundaram, E.V. Proc. Nat. Acad. Sci. India, 1988 58(A)I, 37-42
- [3]. Dawn, H.S., Pitman, T. Young, S.J. Pharm. Sci., 1970, 59, 955.
- [4]. Zucker, L. Hammett, L.P.J. Amer. Chem. Soc., 1939. 61, 79.
- [5]. Y. Hsieh, C. J. G. Duncan, J. M. Brisson, Mass spectro., 21, 629-634, 2007.
- [6]. E. J. Eisenberg, W. M. Eickhoff, J. Chromatogr., 621, 110-114, 1993.
- [7]. M.D.Fusco, M.D. Incalci, D. Gentili, S. Reichert, M. Zuchetti, J. Chromatogr. B, 664, 409-414, 1995.
- [8]. E. Lilimark, B. Pettersson, C. Peterson, J. Lilimark, J. Chromatogr. B, 669, 311-317, 1995.
- [9]. J. M. Redeout, D. C. Ayres, C. K. Lim, T. J. Peters, J. Pharmaceu. Biomed. Anal., 2(1), 125-128, 1984.
- [10]. K. Yamashita, K. Watanbe, H. Takayama, M. Ishibashi, H. Miyazaki, J. Pharmaceu. Biomed. Anal., 15(1), 11-20, 1987.
- [11]. M. A. J. V. Opstal, J. S. Blavw, J. J. M. Holthuis, W. P. V. Bennkom, A. Bult, Analytica Chemi. Act., 202, 35-47, 1987.
- [12]. V. L. Demperio, J. Chromatogr. A, 952, 283-287, 2002.
- [13]. C. L. Chen, F. M. Uckun, J. Chromatogr. B, 744, 91-98, 2000.
- [14]. Littler, J.S. and Waters, W.A.J. Chem. Soc., 1962, 827.
- [15]. Kolthoff, I. and Willman, A.J. Ame. Chem. Soc., 1934, 56, 1007
- [16]. Muhammod, S.S. and Rao, K.V. Bull. chem. soc. Jap., 1963, 36, 943, 949
- [17]. Sharma, V.K., Sharma, K. and Mishra, U. Oxid. commun. 1988, II No. 3-4, 275-284.
- [18]. Sharma, V.K., Sharma, K. and Mishra, U.J. Ind. Chem. Soc., 1986, 63, 586.
- [19]. Sharma, V.K., Sharma, K. and Singh, A. Oxid. Comm., 1990, 13, No.-4, 251-257.
- [20]. Khan, M.U. and Sharma, V.K., Sharma, K. and Dwivedi, H.P. No. 1, 60-65
- [21]. Drummod, A.Y. and Waters, W.A.J. Chem. Soc., 1953, 435.
- [22]. Bartlett, P.D. and Stauffer, C.H. Journal Am. Chem. Soc., 1935, 75, 2580.
- [23]. Srinivasan, V.S. and Venkatsubraman-iam, N. Indian J. Chem., 1976., 14, 488.
- [24]. Valechha, N.D. and Pradhan, A.J. Ind. Chem. Soc., 1984, 61, 945
- [25]. Pechal, M., Holotik, S., Satrasak, M. and Hrusovsky, M. Chem. Zvesti 1983, 37 (2), 159
- [26]. Valechha, N.D. and Pradhan, A.J. Ind. Chem., 1985, 24, 773
- [27]. Meenakshi, A. and Santappa, M.J. Ind. Chem., 1973, II, 393
- [28]. Forsein and Nilsson. "The Chemistry of Carbonyl compous" Zabicky Ed. Inter Science New York 1970, p. (157-240)
- [29]. Wheland Ad. org. chem. III edition John Wiley and sons Inc-Newyork 1979, 56, 502.
- [30]. Amis, E.S.J. Chem. Educat. 1953, 30, 351.
- [31]. Bronsted, J.N.J. Phy. Chem. 1992, 102, 169
- [32]. Grover, V.K. and Gupta, Y.K.J. Inorg. Nucl. chem., 1969, 31, 1403
- [33]. Wiberg, K.B. "Oxidation inorg. chemistry" Academic Press, 1965, chapt. IV
- [34]. Van Helben, R. and Koojiman, E.C. Chem. Abstract, 1961, 55, 17564.

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