Kinetics and Mechanism for the quantitative determination of Acetoacetic ester with N-chlorosaccharin reagent in acetic acid water medium

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Abstract: *The current study gives a kinetics study for the quantitative determination of Acetoacetic ester with N-chlorosaccharin reagent in acetic acid water medium. 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 also described as reaction kinetics, is the study of rates of chemical processes. 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.It has also been highlighted by German Chemist Ludwig-Ferdinand Wilhelmy from his work.

Materials and Methods*: For the kinetic study of oxidation of ethylacetoacetate, diketones and esters i.e. benzoyl acetone, malonic ester, acetyl acetone, by N–Chlorosaccharin. serieThe samples of acetyl acetone (K. light AR) and benzoyl acetone (Emerck) used in this kinetic study with standard grade. The ethyl aceto acetate 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.*

Results*: Relationship between the reaction rate and solvent polarity are described here in detail. The composition of acetic acid water binary mixture has been changed to record the dependence of solvent polarity on the rate of reaction and kinetic data are recorded. From the table it is found that the reaction rate of oxidation process decreases with the increase in the composition of acetic acid. The decrease in reaction rate is probably due to that ethyl aceto acetate/diketone molecule is more stabilized in solution containing large percentage of water than the small percentage of water due to formation of intra molecular hydrogen bond. It is reported 6,7 that extent of enolization is greatly affected by solvent concentration and temperature. Enol is involved in the rate determining step.*

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

I. Introduction

Chemical kinetics also described as reaction kinetics, is the study of rates of chemical processes. 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.[2]

Long before Wilhelmy done out his work, some measurements and the rate of reactions and the mechanism of the reactions. Even then the mechanism cannot be deduced with certainty, since subsequent investigations may reveal unexpected complications. A kinetic study can disprove a mechanism but it cannot establish a mechanism with certainty. The kinetic studies cover a wide range, from several points of view.

The Arrhenius was given a quantitative relationship between temperature and the reaction rate $k = Ae^{-E/RT}$, where A is Frequency factor, R is Gas constant, E is Energy of activation of reaction, k is the rate constant at temp and T is absolute temperature. another relationship between temperature and the reaction rate is given by Eyring and Polanyi, it was derived by applying transition state theory of reaction rate based on statistical-mechanics. This relationship iskr $= \frac{KT}{h}$ K, here kr is the specific rate constant of the reaction at absolute temp (T), K' is boltzmann constant, h is Plank's constant, K is the equilibrium-constant of the reaction. Bronsted[3], Bjerrum[4(a)] and Scatchard[4(b)] were studied the effect of change in the ionic strength on the rate of reaction and derived a relation for dilute solutions. The relation is log k = log k_0 + 1.02 Z_A $Z_B\sqrt{\mu}$for water at 25^0C. where k is rate constant at a given ionic strength (μ) k_0 is The zero ionic strength in obtained when no salt has been added.Z_A and Z_B The suggestion of the reaction is natural species molecule like ZA × ZB will be zero.If one of the reactions is neutral molecule $Z_A × Z_B$ will be zero and the It should be independent in the form of ionic strength, i.e. salt effect II of $Z_A × Z_B$, If $Z_A × Z_B$ is the negative reacting species will have opposite charges, i.e. K will be smaller.The quantum reaction species will have smaller charges it means sufficient is positive hence self study effect will be natural.

II. Material And Methods
For the kinetic study of oxidation of ethylacetoacetate, diketones and esters i.e. benzoyl acetone, malonic ester, acetyl acetone, by N–Chlorosaccharin. serieThe samples of acetyl acetone (K. light AR) and benzoyl acetone (Emerck) used in this kinetic study with standard grade.The ethyl aceto acetate 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.

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.

Preparation of substrate solution has been performed as follows. The substrates viz. acetyl acetone (K. light AR) benzoyl acetone (Emerck) ethyl aceto acetate (Emerck) and malonic ester (VEB) were used for the kinetic oxidation studies. These substrates were very less soluble in water. Hence the preparation of solutions were done by dissolving the required amount of the substrates in the mixture of acetic acid and water having appropriate composition.Preparation of sodium thiosulphate solution and potassium dichromate has been performed as follows. The appropriate weighed amount of BDH sample dissolved in distilled water to prepare the standard solution of potassium dichromae.The standard solution of sodium thiosulphate (hypo) was prepared in the caboratory by dissolving a BDH grade sample in distilled water it was standardized by the use of standard potassium dichromate solution eudiometrically.Preparation of other solutions are wide prepared. The solution of perchloric acid (AR Emerck) and sulphuric acid (AR BDH) was prepared in the laboratory by diluting its appropriate volume by using the distilled water.The concentration of hydrogen ion in both the solutions was estimated by titrating it with standard sodium bydroxide solution using phenolphthalein as in indicator.The solution of sodium perchlorate was prepared by dissolving the requisite amount of Analar (BDH) grade sample in distilled water.For the preparation of binary mixture of different compositions of glacial acetic acid (AR BDH), acetic acid and water was used.The acrylonitrite solution was prepared by the standard procedure for the identification of the free radical formation during the course of oxidation study.
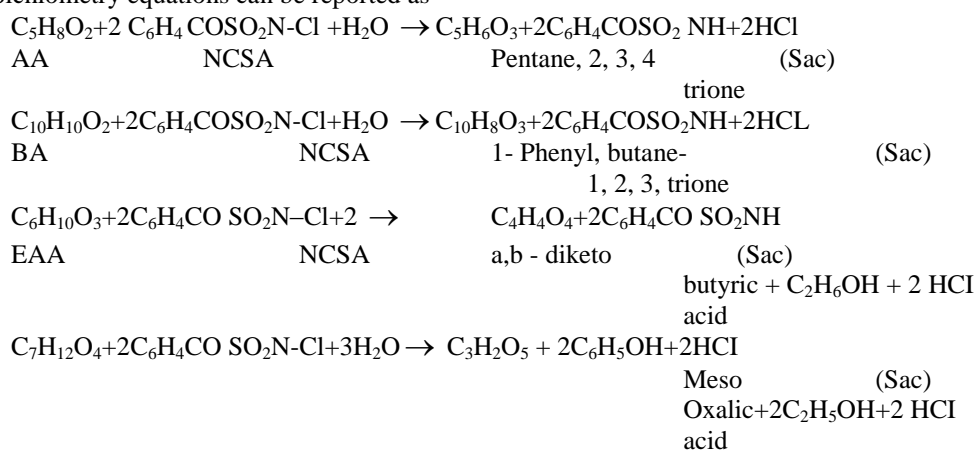
III. Result
A detailed survey of the experimental results clearly show that, the oxidation of acetyl acetone at room temperature in acetic acid-water medium with NCSA is slightly fast, but can be measured while that of benzoyl acetone and both the esters proceed at a negligible speed and hence their oxidation was carried out at higher temperature (BA – 55^0C , EAA- 60^0C and ME - 60^0C).

Preliminary studies reveal that both the dike tones like those of esters follow first order kinetics with respect to NCSA under the conditions when concentration of Substrate is greater than NCSA, all these reactions are homogeneous. The reactions of benzoyl acetone, ethyl aceto acetate and malonic ester with NCSA are characterized by an induction period. The induction period has been accounted as the slow approach of the complexes in the activated form to a steady state condition.

Features for the oxidation of diketones and esters with N–Chlorosaccharin are as follows. The oxidation follows first order kinetics with respect to NCSA. The reaction rate gradually increases at its very high concentration. The order of reaction with respect to substrate is unity. Kinetic study also provides evidence for complex formation between oxidant and substrate.Addition of saccharin retards the reactions rate. Primary salt does not exhibit any effect on reaction rate.The rate of reaction is accelerated with increasing the concentration of perchloric acid.The reaction rate decreases with rise in percentage composition of medium of the solvent.The formation of intermediate at transition state in the enolic form of substrate species.The result obtained on the basis of above data, predicts probable reaction path, which is as follows.

Stoichiometry and product analysis have been performed. The stoichiometry of each reaction has been analysed seperately.and it was observed that, 2-3 moles of oxidant consumed 1 mole of substrate for complete oxidation.The stoichiometry equations can be reported as

$$C_5H_8O_2 + 2\ C_6H_4COSO_2N\text{-}Cl + H_2O \rightarrow C_5H_6O_3 + 2C_6H_4COSO_2\ NH + 2HCl$$

AA   NCSA   Pentane, 2, 3, 4   (Sac)

trione

$$C_{10}H_{10}O_2 + 2C_6H_4COSO_2N\text{-}Cl + H_2O \rightarrow C_{10}H_8O_3 + 2C_6H_4COSO_2NH + 2HCL$$

BA   NCSA   1- Phenyl, butane-   (Sac)

1, 2, 3, trione

$$C_6H_{10}O_3 + 2C_6H_4CO\ SO_2N\text{–}Cl + 2 \rightarrow C_4H_4O_4 + 2C_6H_4CO\ SO_2NH$$

EAA   NCSA   a,b - diketo   (Sac)

butyric + C_2H_6OH + 2 HCl
acid

$$C_7H_{12}O_4 + 2C_6H_4CO\ SO_2N\text{-}Cl + 3H_2O \rightarrow C_3H_2O_5 + 2C_6H_5OH + 2HCl$$

Meso   (Sac)

Oxalic + $2C_2H_5OH$ + 2 HCl
acid

The oxidation products were identified qualitatively. Trione is obtained as product of oxidation of acetyl acetone and benzoyl acetone, whereas aceto aetic ester and malonic ester are oxidized in to α, β- diketo butyric acid and meso oxalic acid respectively.

In selenium dioxide oxidation of acetyl acetone and benzoyl acetone[1] trione was reported as oxidation product whereas α, β- diketo butyrate was reported as oxidative product of ethyl aceto acetate[2] for the selenium dioxide oxidant.

Dependence of rate on oxidant are as follows. A series of experiments were performed with acetyl acetone, benzoyl acetone, ethyle aceto acetate and diethyl malonate 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 table clearly 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. In NCSA oxidative study of esters i.e. ethyl aceto acetate and diethyl malonate, the reaction follow first order kinetics. The induction period does not depend on the concentration of NCSA. The constancy does not depend on the concentration of NCSA. The constancy in values of first order rate constant and the linear plots with nearly same slope value leads that, both the esters show first same slope value leads that, the two esters predicts the first order kinetics for the oxidant within induction period.

According to Santappa[3] et. al., oxidation of methyl ethyl ketone and cyclopentanone exhibits first order dependence on [TI III] and 3–Pentanone[4]–TI (III) oxidation obeys kinetic equation of pseudo first order.

Relationship between the reaction rate and solvent polarity are described as follows. The composition of acetic acid water binary mixture has been changed to record the dependence of solvent polarity on the rate of reaction and kinetic data are recorded. From the table it is found that the reaction rate of oxidation process decreases with the increase in the composition of acetic acid.The decrease in reaction rate is probably due to that ethyl aceto acetate/diketone molecule is more stabilized in solution containing large percentage of water than the small percentage of water due to formation of intra molecular hydrogen bond. It is reported[6,7] that extent of enolization is greatly affected by solvent concentration and temperature. Enol is involved in the rate determining step.

Primary salt effect. The primary salt effect on the reaction rate has been carried out by adding neutral salt such as sodium perchlorate. The data is reported, show that the one of the reactants should have participated and it must be neutral molecule present in the rate.
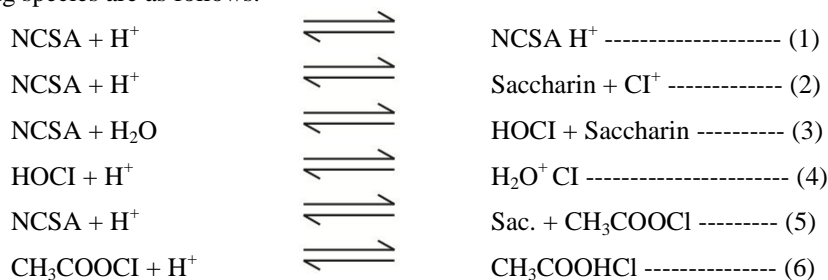
IV. Discussion

The above study leads to the following. The order with respect to N–Chlorosaccharin is unity.The order with respect to diketones and esters falls from 1 to 0 i.e. the rate of oxidation is independent of at higher concentration of diketones and keto esters.There is an evidence for the formation of complex between diketones and esters with the oxidant species.Retardation trend of saccharin indicates that the oxidant is in pre-equilibrium with saccharin and finally helps in deciding the nature of reactive species of the reactants. This type of observation is common in certain oxidation reactions with metal ions like Ce (IV)[10], TI (III)[11], Mn (III)[12] and NBSA[13a,b,c] and NCSA[14] etc.

It is reported in literature that the oxidation of all the active methylene compounds involved under investigation acceleration of reaction rate added perchloric acid rules out hydrolytic product as active oxidant, but in aqueous acetic acid, there is every possibility that the electrophilic species may be free ions 15.

It has been mentioned that the molecular NBSA and NCSA or their hydrolytic product HOBr[13] (a,b,c) and HOCl[16] exists as an active form of species in aqueous acetic acid medium.
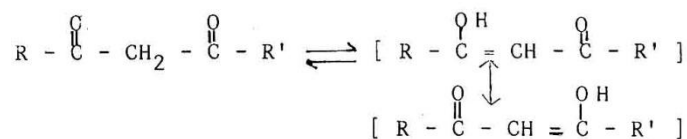NCSA like other N-halo oxidants may exist in presence of H^+ yielding a protonated species viz. NCSA H^+, H_2O^+ Cl (hypochorous acidium ion, a electrolyte and an oxidant) or CI^+ as an active oxidizing species. The oxidizing species are as follows.

$$NCSA + H^+ \rightleftharpoons NCSA\ H^+ \quad \text{-------------------- (1)}$$

$$NCSA + H^+ \rightleftharpoons Saccharin + CI^+ \quad \text{------------- (2)}$$

$$NCSA + H_2O \rightleftharpoons HOCI + Saccharin \quad \text{---------- (3)}$$

$$HOCI + H^+ \rightleftharpoons H_2O^+ CI \quad \text{----------------------- (4)}$$

$$NCSA + H^+ \rightleftharpoons Sac. + CH_3COOCl \quad \text{--------- (5)}$$

$$CH_3COOCI + H^+ \rightleftharpoons CH_3COOHCl \quad \text{--------------- (6)}$$

The formation of reacting species can be explained on the basis of kinetic results.
(a)   The addition of perchloric acid not retards the rate of oxidation there by eliminating the involvement of protonated oxidant species.
(b)   The retardation of reaction rate with addition of saccharin to the reaction mixture suggest that the pre-equilibrium step must process a process in where saccharin can be one of the product. This fact also rules out the possibility of NCSA and NCSA H^+ is the reacting species.
(c)   The retardation of rate with increasing percentage composition of acetic acid further discards the possibility of acetate complex of NCSA as the reacting species.

Owing to the extreme electronegative character of Carboxyl functional group the a-C-H bond are weakened as the electrons are displaced towards the carbon atom resulting in the loss of one of the a-C-H as a proton. This explains the usual reactivity of the methylene group placed either adjacent to the carbonyl group or sandwiched in between two carbonyl groups. Such an activation is characteristic of ketones, aldehydes, esters and active methylene compounds towards a number of reactions such s substitution, oxidation, addition etc. through enol and enolate ion formation. The carbonyl compounds exist in keto-enol equilibrium and the enol content is depend on the nature of solvents, resonance and hydrogen bonding the carbonyl compounds under study are 1,3- di carbonyl compounds treated as part of ester groups in esters. The methylene group is between two electron attracting carbonyl groups. So, that the group is highly acidic, enolized rapidly and is stabilized by resonance as :

$$R - \overset{O}{\underset{\|}{C}} - CH_2 - \overset{O}{\underset{\|}{C}} - R' \rightleftharpoons [\ R - \overset{O\ H}{\underset{}{C}} = CH - \overset{O}{\underset{\|}{C}} - R'\ ]$$

$$[\ R - \overset{O}{\underset{\|}{C}} - CH = \overset{O\ H}{\underset{|}{C}} - R'\ ]$$

Where R and R' are CH_3 for AA, R is $-C_6H_5$ and R' is CH_3 for BA, R is $-CH_3$ and R' is OC_2H_5 for EAAandR and R' is $-O-C_2H_5$ for ME. The enol form of acetyl acetone and ethyl acetoacetate is stabilized by intra molecular hydrogen bonding.
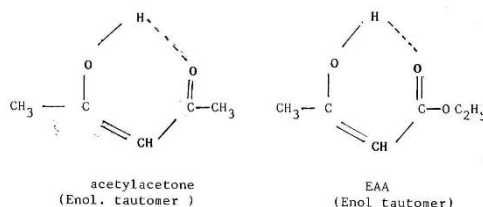
Enolisation is an acid and base catalyzed reaction. The process goes through concentering or push-pull mechanism. Acid catalyzed enolisation of carbonyl compound follow two major steps (1) the protonation of Carbonyl functional group and (II) process of deprotonation for a-carbon of the conjugate acid. The aforesaid for going factor are operative on structural effects. Enol as the reactive species was reported in the oxidation of diketones by TI (III) [3] Hg (II) [19] and manganic pyrophosphate.[20] According to Litter and Waters two electrons oxidant attack enol form rather than keto form. The rate of enolisation of ketones are measured by halogenation[21] method.

Under the identical experimental conditions the rate of bromination of acetyl and benzoyl acetone is very slow and hence the rate of enolisation may be considered as rate-determining step. In ester oxidation the rate of bromination follows first order kinetics and the pseudo first order rate constant for bromination is nearly some to the oxidation rate i.e.k_{Br} (EAA) is 15.93×10^{-3} min^{-1}, k_{ox} (EAA) is 17.53×10^{-3} min^{-1}and k_{Br} (ME) is 14.62×10^{-3} min^{-1}, k_{ox} (ME) $= 16.46 \times 10^{-3}$ min^{-1}. The enolisation has been reported as rate determining step in TI (III) oxidation of cyclohaxanone[22], Mn(II) oxidation of acetophenone[23], phenyl iodoso acetate oxidation of ketones[24], lead tetra acetate oxidation of acetyl acetone, ethyl aceto acetate and diethyl malonate[25].Oxidation of all four carbonyl compounds are acid catalyzed reaction.Enhancement of rate with addition of perchloric acid is mainly due to the increase in enol content.The plot of k_{obs} versus [HClO$_4$] for each compound is with increase in acetic acid concentration in aqueous acetic acid medium indicating dipole-dipole interaction.

V. Conclusion

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

References

[1].   Valechha, N.D. and Pradhan, A.J. Ind. Chem. Soc., 1984, 61, 945
[2].   Valechha, N.D. and Pradhan, A.J. Ind. Chem., 1985, 24, 773
[3].   Meenakshi, A. and Santappa, M.J. Ind. Chem., 1973, II, 393
[4].   Pechal, M., Holotik, S., Satrasak, M. and Hrusovsky, M.Chem. Zevesti 1983, 37 (2), 159
[5].   Kolthoff, I. and Willman, A.J. Ame. Chem. Soc., 1934, 56, 1007
[6].   Forsein and Nilsson."The Chemistry of Carbonyl compous" Zabicky Ed. Inter Science New York 1970, p. (157-240)
[7].   WhelandAd. org. chem. III edition John Wiley and sons Inc-Newyork 1979, 56, 502.
[8].   Amis, E.S.J. Chem. Educt. 1953, 30, 351.
[9].   Bronsted, J.N.J. Phy. Chem. 1992, 102, 169
[10].   Grover, V.K. and Gupta, Y.K.J. Inorg. Nucl. chem., 1969, 31, 1403
[11].   Wiberg, K.B. "Oxidation inorg. chemistry" Academic Press, 1965, chapt. IV
[12].   Muhammod, S.S. and Rao, K.V.Bull. chem. soc. Jap., 1963, 36, 943, 949
[13].   Sharma, V.K., Sharma, K. and Mishra, U.Oxid. commun. 1988, II No. 3-4, 275-284.
[14].   Sharma, V.K., Sharma, K and Mishra, U.J. Ind. Chem. Soc., 1986, 63, 586.
[15].   Sharma, V.K., Sharma, K. and Singh, A.Oxid. Comm., 1990, 13, No.-4, 251-257.
[16].   Khan, M.U. and Sharma, V.K., Sharma, K. and Dwivedi, H.P.No. 1, 60-65
[17].   Briody, J.M. and Moore, R.A.J. Chem. So., 1972. 179.
[18].   Raghunath Rao, P. and Sundaram, E.V.Proc. Nat. Acad. Sci. India, 1988 58(A)I, 37-42
[19].   Dawn, H.S., Pitman, T. Young, S.J. Pharm. Sci., 1970, 59, 955.
[20].   Zucker, L. Hammett, L.P.J. Amer. Chem. Soc., 1939. 61, 79.
[21].   Littler, J.S. and Waters, W.A.J. Chem. Soc., 1962, 827.
[22].   Drummod, A.Y. and Waters, W.A.J. Chem. Soc., 1953, 435.
[23].   Bartlett, P.D. and Stauffer, C.H.Journal Am. Chem. Soc., 1935, 75, 2580.
[24].   Srinivasan, V.S. and Venkatsubraman-iam, N.Indian J. Chem., 1976., 14, 488.
[25].   Van Helben, R. and Koojiman, E.C.Chem. Abstract, 1961, 55, 17564.