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Oxidative Degradation of Methyl Ethyl Ketone by N-Chlorosaccharin

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The oxidative feature of methyl ethyl ketone has been carried out with N-chlorosaccharin (NCSA) in aqueous acetic acid medium in presence of H^+ ions. The dx/dt is a direct function of first power of concentration of oxidant (NCSA) and one to zero power of methyl ethyl ketone and acid. The reaction was found to decrease by the increasing concentration of reduction product saccharin and acetic acid. The reactive species H_2O^+Cl has been actively participated in 1 : 2 mole ratio with enolic ketone and exhibited complex nature of the reaction.

Key Words: Oxidimetric, Degradation, Halo-oxidant, N-chloro-saccharin.

INTRODUCTION

Bacchawat and Mathur[1] developed N-chlorosaccharin (NCSA) as a potential (+1.201 V) titrant for the oxidimetric determination of some typical reductants in aqueous acid medium. NCSA is a moderately strong oxidant with two-electron system. Now-a-days, NCSA has drawn the attention of several laboratories due to its non-hazardous nature and its ability to produce halonium ion, rather than halogen-free radicals. It is a good and fertile halo-oxidant stabilized by electron localization[2]. Oxidation of ketones has been explored widely with different oxidants, *viz.*, CAT[3], NBSA[4], $KMnO_4$[5], LTA[6], SeO_2[7], chromic acid[8], Ce(IV)[9], V(v)[10], Tl(III)[11] and more recently the results of kinetics emanated from our laboratory with NCSA[12]. The work is scanty and this inspired us to report here, as a note, the oxidation of methyl ethyl ketones utilizing NCSA in aqueous acetic acid medium.

EXPERIMENTAL

Methyl ethyl ketone employed was commercially available (Sigma). All other chemicals used were of AnalaR grade. The stock solution of the substrate was prepared in purified glacial acetic acid as and when required. Doubly distilled water was used throughout. The kinetic measurements were made under pseudo first-order condition by maintaining [Substrate] $\gg$ [Oxidant]. The reaction was initiated by adding requisite amount of solutions of substrate to the NCSA solution containing acetic acid, water and H^+ ions, both being equilibrated in a thermostatic bath. The unreacted NCSA was estimated iodometrically. The duplicate kinetic runs showed reproducible results of rate constants within ±2%.

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RESULTS AND DISCUSSION

The stoichiometric results established that 1 mole of ketone reacted with 2 moles of NCSA. The product of the oxidation was ascertained to be done from the formation of 2,4-diphenyl hydrazone (DNP) and also identified by paper chromatography.

The plots of log (a–x) *vs.* time were linear showing first-order dependency with respect to [NCSA] and one to zero order for substrate. The plot of $1/k_{obs}$ *vs.* 1/[substrate] was linear with positive intercept on y-axis (Fig. 1, Table-1) indicating the possibility of formation of a long lived intermediate during the oxidation with enolic species of substrate. The effect of $[H^+]$ was studied using perchloric acid. The observation led to the conclusion that the reaction is acid catalyzed. The plot of k_1 *vs.* $[HClO_4]$ is not linear (Fig. 2, Table-2). The study revealed that order falls from one to zero at higher concentration of acid.

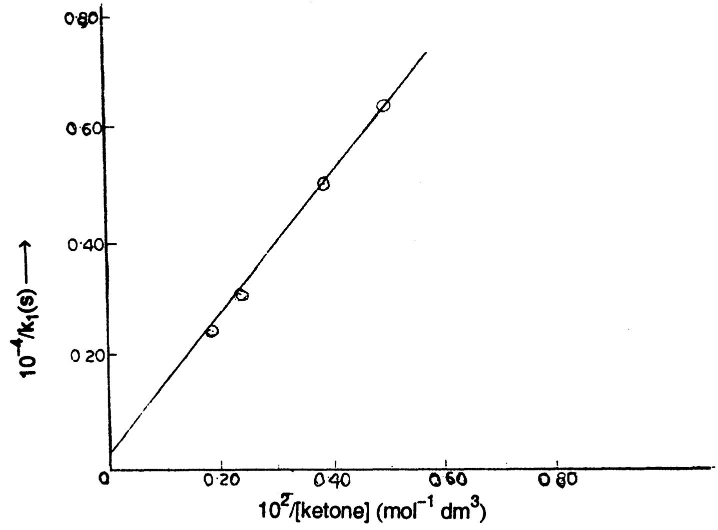


Fig. 1. Effect of rate on the $[CH_3CH_2COCH_3]$, plot of k_1^{-1} *vs.* $[ketone]^{-1}$, [NCSA] = 2.50×10^{-3} (mol dm^{-3}), $[H^+]$ = 0.05 (mol dm^{-3}), $HOAc\text{-}H_2O$ = 20% (v/v), temperature = 323 K

TABLE-1
DEPENDENCE OF RATE ON THE CONCENTRATION OF METHYL ETHYL KETONE

S.No.	[substrate] × 10^2 (mol dm^{-3})	10^4 k_1 (s^{-1})
1.	1.25	1.42
2.	2.00	1.54
3.	2.50	1.95
4.	4.00	2.83
5.	5.00	3.58

[NCSA] = 2.50×10^{-3} (mol dm^{-3}); $[H^+]$ = 5.0×10^{-2} (mol dm^{-3}); $HOAc\text{-}H_2O$ = 20% (v/v); Temperature = 323 K

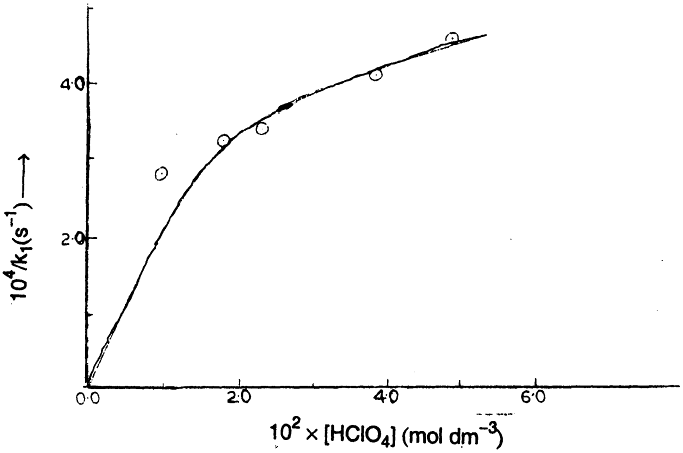


Fig. 2. Effect of rate on the [$HClO_4$], plot of k_1 *vs.* [$HClO_4$], [NCSA] = 2.50×10^{-3} (mol dm^{-3}), [$CH_3CH_2COCH_3$] = 2.50×10^{-2} (mol dm^{-3}), HOAc-H_2O = 20% (v/v), temperature = 323 K

TABLE-2
DEPENDENCE OF RATE ON THE CONCENTRATION OF ACID

S.No.	[H^+] × 10^2 (mol dm^{-3})	$10^4 k_1$ (s^{-1})
1.	0.50	1.950
2.	1.00	2.920
3.	2.00	3.380
4.	2.50	3.460
5.	4.00	4.164
6.	5.00	4.765

[NCSA] = 2.50×10^{-3} (mol dm^{-3}); [methylethylketone] = 2.50×10^{-2} (mol dm^{-3}); HOAc-H_2O = 20% (v/v); Temperature = 323 K

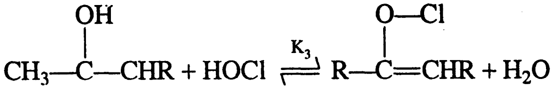
The polarity of the medium was varied by using different percentage of acetic acid and water binary mixture. The rate was found to be decreased with increasing percentage of acetic acid. The addition of primary salt ($NaClO_4$) slightly alters the rate constant, while presence of saccharin retards the rate of reaction as evidenced by linear plot of 1/k *vs.* [saccharin]. The study rules out the formation of any free radicals by the addition of acrylonitrile (monomer). H_2O^+Cl as a profile reacting species of oxidant with enolic form of the substrate measures its rate.

Mechanism

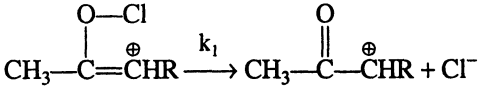
A probable mechanism for the oxidation of methylethyl ketone in aqueous acetic acid medium can therefore be formulated as

$$\text{NCSA} + H_2O \overset{K_1}{\rightleftharpoons} \text{HOCl} + \text{Saccharin} \qquad (1)$$

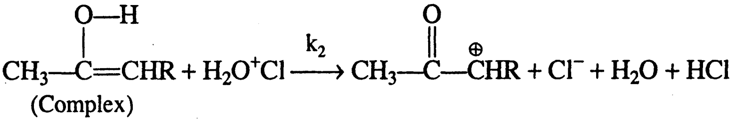
$$HOCl + H^+ \overset{K_2}{\rightleftharpoons} H_2O^+Cl \tag{2}$$



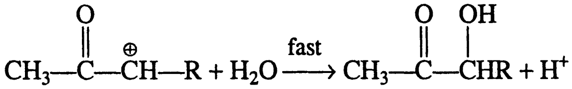
$$CH_3-\overset{\overset{\displaystyle OH}{|}}{C}-CHR + HOCl \overset{K_3}{\rightleftharpoons} R-\overset{\overset{\displaystyle O-Cl}{|}}{C}=CHR + H_2O \tag{3}$$



$$CH_3-\overset{\overset{\displaystyle O-Cl}{|}}{C}=\overset{\oplus}{C}HR \xrightarrow{k_1} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\oplus}{C}HR + Cl^- \tag{4}$$



$$\underset{\text{(Complex)}}{CH_3-\overset{\overset{\displaystyle O-H}{|}}{C}=CHR} + H_2O^+Cl \xrightarrow{k_2} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\oplus}{C}HR + Cl^- + H_2O + HCl \tag{5}$$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\oplus}{C}H-R + H_2O \xrightarrow{\text{fast}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle OH}{|}}{C}HR + H^+ \tag{6}$$

The above mechanism leads to the following rate law:

$$k_{obs} = \frac{[\text{enol}]\{K_1K_3k_1 + K_1K_2k_2[H^+]\}}{[\text{Sac}] + K_1 + K_1K_2[H^+] + K_1K_3[\text{enol}]} \tag{7}$$

This rate law explains all the observed experimental facts.

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