Asian Journal of Chemistry Vol. 15, No. 2 (2003), 595–600

Kinetic and Mechanistic Investigation of N-chlorosaccharin Oxidation of 2-Alkanones

SHAHNAZ KHAN*, M.U. KHAN, SANJAY KUMAR SINGH†,
H.D. GUPTA† and P.K. SINGH‡
Department of Chemistry, Government Model Science College, Rewa-486 001, India

N-Chlorosaccharin (NCSA) oxidation of 2-alkanones is investigated in aqueous acetic acid and perchloric acid medium. The reactions exhibit first order dependence in oxidant [NCSA]. The order of the reactions with respect to substrate and perchloric acid varies from one to zero. The reaction velocity retards by the addition of saccharin and rising percentage of binary mixture of acetic acid and water whereas primary salt shows slightly increasing trends in kinetic rate. The stoichiometric studies revealed 1 : 2 mole ratio with complex mechanism.

Key Words: Kinetic, Mechanistic, N-Chlorosaccharin oxidation, 2-Alkanones.

INTRODUCTION

Recently reactions involving N-chlorosaccharin (NCSA) received limited attention[1,2]. Although some investigations utilising NCSA on oxidation kinetics in hydroxy acids3, 4, alcohols[5, 6], aldehydes[7,] ketones[8], etc. in aqueous acetic acid in presence of perchloric acid medium have been reported.

A survey of literature pertaining to the oxidation kinetics studies of 2-alkanones (2-butanone, 2-pentanone, 2-heptanone and 2-octanone) employing NCSA has not been done so far. This prompted the authors to undertake the task of probing the hitherto unreported results in the present communication.

EXPERIMENTAL

The sample of NCSA used in this study was prepared in acetic acid (BDH). All other chemicals were of Sigma, GR or AnalaR grade. The solutions used were standardized iodometrically[9.] The solutions of the 2-alkanones were prepared in requisite volume of acetic acid-water mixture. The kinetics measurements were initiated by mixing appropriate volumes of two solutions (both being pre-equilibrated at the reaction temperatures) containing NCSA solution and the 2-alkanones (organic substrate) in acetic acid-water mixture in presence of $HClO_4$. The progress of the reaction was monitored by estimating unconsumed NCSA iodometrically.

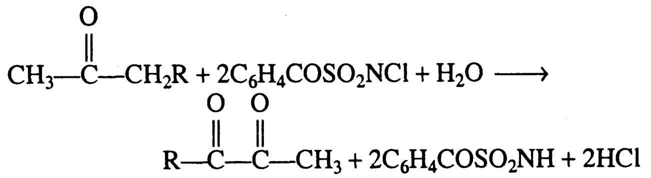
The stoichiometric results indicated consumption of mole ratio 1 : 2 as represented by the following empirical equation:

---

*For correspondence: Opposite I.G. Police Office, Civil Lines, Rewa-486 001, India..

†Government T.R.S. Excellence College, Rewa-486 001, India.

‡Government S.G.S. College, Sidhi (M.P.), India.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2R + 2C_6H_4COSO_2NCl + H_2O \longrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3 + 2C_6H_4COSO_2NH + 2HCl \qquad (1)$$

where R = —CH_3; —C_2H_5, —C_4H_9 and —C_5H_{11}, for 2-butanone, 2-pentanone, 2-heptanone and 2-octanone respectively.

The corresponding diones and saccharin were found as the common products of oxidation and were identified by paper chromatography, spot test and also by forming their 2-4-dinitrophenyl hydrazones.

RESULTS AND DISCUSSION

The kinetics of oxidation of 2-alkanones follows the first-order with respect to oxidant under the condition [NCSA] ≪ [2-alkanones][H^+], which is evidenced by the linear plots of log (a – x) *vs.* time for different initial concentrations of oxidant in each case of 2-alkanones (Fig. 1, Table-1).

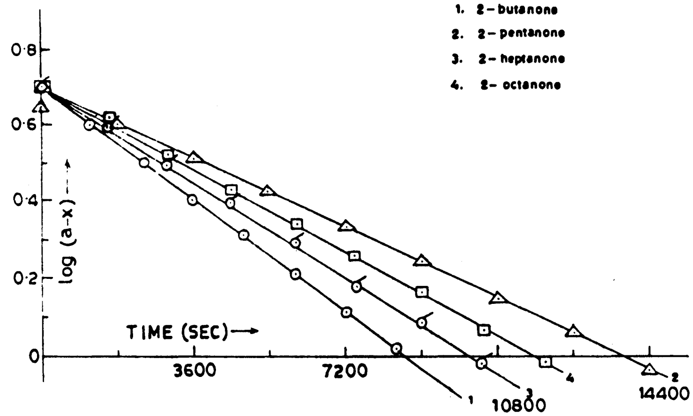


Fig. 1. Dependence of rate on the initial concentration of NCSA: Plot of log (a – x) *vs.* time. 10^3 [NCSA] (mol dm^{-3}) = 2.5 (1–4); 10^2 [2-alkanones] (mol dm^{-3}) = 2.5 (1–4); [H^+] (mol dm^{-3}) = 0.05 (1–4); HOAc-H_2O % (v/v) = 20 (1–4); Temperature K = 323

TABLE-1

DEPENDENCE OF RATE ON THE INITIAL CONCENTRATION OF NCSA

S.No.	[NCSA] × 10^3 (mol dm^{-3})	10^4 k_1 (s^{-1})			
		2-butanone	2-pentanone	2-heptanone	2-octanone
1.	1.00	1.909	1.194	1.295	1.397
2.	2.00	1.938	1.156	1.301	1.409
3.	2.50	1.956	1.760	1.340	1.368
4.	4.00	1.918	1.086	1.350	1.412
5.	5.00	1.945	1.036	1.462	1.427

10^2 [Substrate] (mol dm^{-3}) = 2.5 (1–4); [H^+] (mol dm^{-3}) = 0.05 (1–4); HOAc-H_2O % (v/v) = 20 (1–4); Temperature K = 323 (1–4)

The plot of k_1 *vs.* [substrate] is linear at low concentration of substrate, but the order falls as the curves tend towards x-axis at higher concentration (Fig. 2). The double reciprocal plot between k_1^{-1} *vs.* $[\text{substrate}]^{-1}$ is linear with positive intercept on y-axis (Fig. 3) indicating and providing confirmatory evidence about the formation of a complex between oxidant and enolic species of substrate.

The reactions are acid catalyzed. The order with respect to $[H^+]$ is one at lower concentration but tends to zero as the curves attain the limiting rate at higher concentration of $[H^+]$.

Variation in the dielectric constant of the medium suggests that rate decreases with increasing percentage of acetic acid; this fact is supported by the plot of log k *vs.* 1/D, which gives negative slope (Fig. 2, Table-2).

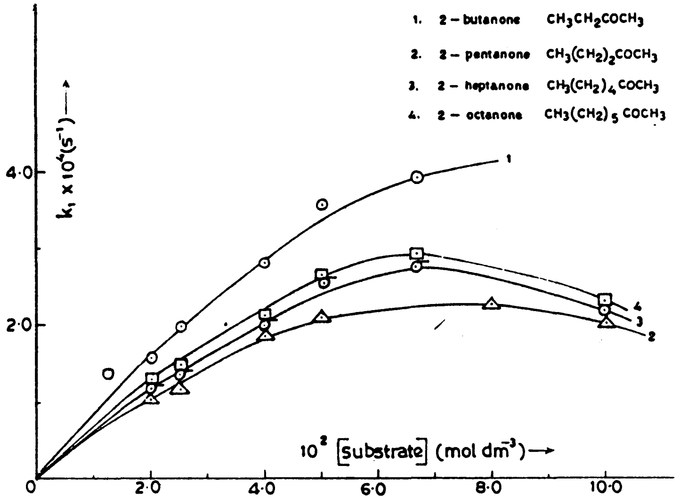


Fig. 2. Dependence of rate on the concentration of 2-alkanones: Plot of k_1 vs. [2-alkanones] 10^3 [NCSA] (mol dm^{-3}) = 2.50 (1–4); $[H^+]$ (mol dm^{-3}) = 0.50 (1–4); $HOAc\text{-}H_2O$ % (v/v) = 20 (1–4); Temperature K = 323 (1–4)

TABLE-2
DEPENDENCE OF RATE ON DIELECTRIC CONSTANT OF THE MEDIUM

S.No.	$HOAc\text{-}H_2O$ % (v/v)	10^3/D	10^4 k_1 (s^{-1})			
			2-butanone	2-pentanone	2-heptanone	2-octanone
1.	10	15.50	2.651	1.459	1.566	1.481
2.	15	16.35	—	1.321	—	—
3.	20	17.17	1.956	1.1766	1.340	1.368
4.	30	19.15	1.558	1.021	1.218	1.185
5.	40	21.98	1.257	0.985	1.229	1.083

10^2 [NCSA] (mol dm^{-3}) = 2.50 (1–4) and other conditions are same as in Table-1.

The effect of primary salt on the reaction rate by the addition of $NaClO_4$ is that a slight increasing rate of oxidation is observed, whereas the added saccharin retards the rate of the reaction. The reactions under study fail to induce polymerisation with added acrylonitrile (monomer).

The values of various Arrhenius-Eyring thermodynamic parameters have been evaluated from the study of rate measurements at different temperatures for the systems and are presented in Table-3.

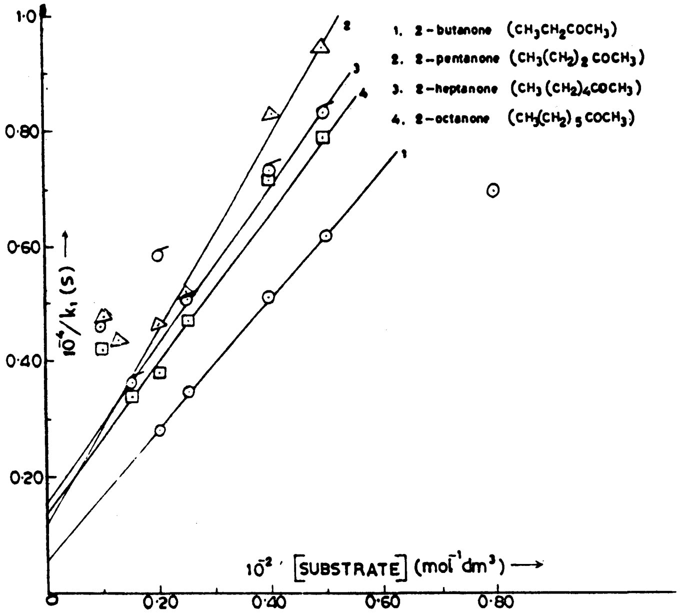


Fig. 3. Dependence of rate on the concentration of 2-alkanones: Plot of k_1 vs. $[substrate]^{-1}$ $[NCSA] \times 10^{-3}$ ($mol\ dm^{-3}$) = 2.50 (1–4); $[H^+]$ ($mol\ dm^{-3}$) = 0.05 (1–4); $HOAc-H_2O$ % (v/v) = 20 (1–4); Temperature K = 323 (1–4)

TABLE-3
VARIOUS THERMODYNAMIC PARAMETERS

S.N.	Substrate	E (kJ mol^{-1})	A (s^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	$-\Delta H^{\#}$ (kJ mol^{-1})
1.	2-butanone	70.260 ±0.662	3.554 $\pm 0.064 \times 10^7$	65.419 ±0.305	92.584 ±0.561	83.462 ±0.066
2.	2-pentanone	75.153 ±0.657	7.904 $\pm 0.312 \times 10^7$	65.431 ±0.0427	93.970 ±0.262	87.682 ±0.835
3.	2-heptanone	74.135 ±0.533	1.294 $\pm 0.003 \times 10^8$	66.833 ±0.668	93.810 ±0.308	83.183 ±0.003
4.	2-octanone	72.557 ±0.111	7.389 $\pm 0.039 \times 10^8$	64.625 ±0.293	93.537 ±0.459	88.820 ±0.078

On the basis of the aforementioned concise results on the kinetics of oxidation of 2-alkanones NCSA system, it would be most appropriate at this stage to discuss the actual reacting species of NCSA as follows:

$$\mathrm{NCSA + H_2O \rightleftharpoons HOCl + Saccharin} \quad (2)$$

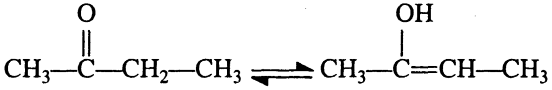
$$\mathrm{HOCl + H^+ \rightleftharpoons H_2O^+Cl} \quad (3)$$

$$\mathrm{NCSA + H^+ \rightleftharpoons NCSAH^+} \quad (4)$$

$$\mathrm{NCSAH^+ + H_2O \rightleftharpoons H_2O^+Cl + Saccharin} \quad (5)$$

Since the present investigation is carried out in acetic acid medium containing perchloric acid, the involvement of protonated HOCl results in a hypochlorous acidium ion H_2O^+Cl, a prime cationic chlorine species, which is a stronger electrophile and a remote profile of the choice.

The reactive species of substrate (2-alkanone) may be determined by enolization; which is an acid as well as base catalyzed reaction and proceeds by a concerted or push-pull mechanism. The enolisation of 2-butanone (methyl ethyl ketone) may be formulated as:

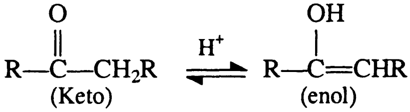


$$\mathrm{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_3 \rightleftharpoons CH_3{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}CH{-}CH_3} \quad (6)$$

Tlie rate of enolization was determined by bromination method for the system under investigation and was found much faster than the rate of oxidation. Hence enol form of 2-alkanones is probably participating in the rate determining step. Enol as a reactive species of the substrates has also been reported in oxidations by two electron oxidants such as Tl(III)[10], Hg(II)[11] etc. It is further supported by Wiberg and Schaefer[12] who regarded enol as a hydroxy compounds in the chromic acid oxidation of alcohols. The view also gains support from the ampoule of evidence that enhancement of rate with $HClO_4$ is mainly due to the increase in the enol content which occurs *via* the conjugate acid species[13].

Mechanism

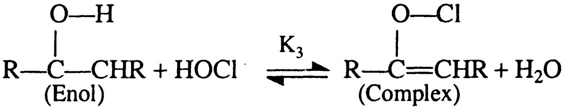
In the present investigation, the powerful reactive species H_2O^+Cl interacts with the enolic form of substrate in the slow process to form a complex. The probable mechanism for the oxidation of 2-alkanones with NCSA could be proposed as per the following scheme:



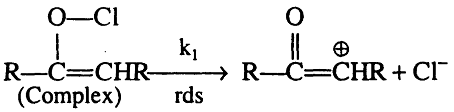
$$\underset{\text{(Keto)}}{\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2R}} \overset{H^+}{\rightleftharpoons} \underset{\text{(enol)}}{\mathrm{R{-}\overset{\overset{\displaystyle OH}{|}}{C}{=}CHR}} \quad (7)$$

$$\mathrm{NCSA + H_2O} \overset{K_1}{\rightleftharpoons} \mathrm{HOCl + saccharine} \quad (8)$$

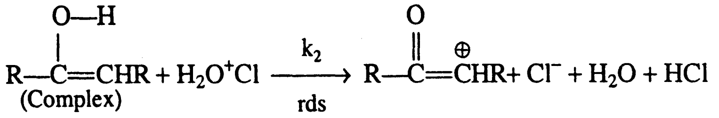
$$\mathrm{HOCl + H^+} \overset{K_2}{\rightleftharpoons} \mathrm{H_2O^+Cl} \quad (9)$$



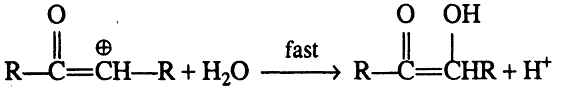
$$\underset{\text{(Enol)}}{\mathrm{R{-}\overset{\overset{\displaystyle O{-}H}{|}}{C}{-}CHR}} + \mathrm{HOCl} \overset{K_3}{\rightleftharpoons} \underset{\text{(Complex)}}{\mathrm{R{-}\overset{\overset{\displaystyle O{-}Cl}{|}}{C}{=}CHR}} + \mathrm{H_2O} \quad (10)$$



$$\underset{\text{(Complex)}}{\mathrm{R{-}\overset{\overset{\displaystyle O{-}Cl}{|}}{C}{=}CHR}} \xrightarrow[\text{rds}]{k_1} \mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{=}CHR}^{\oplus} + \mathrm{Cl^-} \quad (11)$$



$$\underset{\text{(Complex)}}{R{-}\overset{\overset{\displaystyle O{-}H}{|}}{C}{=}CHR} + H_2O^+Cl \xrightarrow[\text{rds}]{k_2} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{=}\overset{\oplus}{C}HR + Cl^- + H_2O + HCl \qquad (12)$$



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{=}\overset{\oplus}{C}H{-}R + H_2O \xrightarrow{\text{fast}} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{=}\overset{\overset{\displaystyle OH}{|}}{C}HR + H^+ \qquad (13)$$

Taking into consideration the various steps involved in the proposed scheme of the mechanism, the rate law could be derived as:

$$K_{obs} = \frac{\text{Rate}}{[\text{NCSA}]_T} = \frac{[\text{enol}]\{K_1K_3k_1 + K_1K_2k_2[H^+]}{[\text{Sac}] + K_1 + K_1K_2[H^+] + K_1K_3\,[\text{enol}]} \qquad (14)$$

The rate law is apparently capable of explaining and justifying all the observed facts at low and high concentrations of substrates.

The observed order of reactivity among the 2-alkanones studied is 2-butanone > 2-octanone > 2-heptanone> 2-pentanone. The fastest rate of 2-butanone may be attributed to the side reaction[14] and the existing dormancy of steric, inductive and hyperconjugative effects, among the molecules is the main reason for the above order of reactivity. The 2-octanone exhibits slightly slower rate than 2-pentanone which is probably due to the enhanced + I effect of $—CH_2—(CH_2)_3—CH_3$ chain.

It increases the electron density on the chain, which subsequently checks the loss of protons. A similar order of reactivity has also been reported in SeO_2 oxidation of 2-alkanones[15].

The fairly constant value of $\Delta G^{\#}$ affords the support for prevailing of similar operative mechanisms. The high negative value of $\Delta S^{\#}$ (–83.462 JK mol^{-1}) suggests the rigid complex forming ability of H_2O^+Cl with ketone in the transition state. The iso-kinetic temperature β is 361 K well above the experimental temperature, indicating that the reactions are enthalpy controlled.

REFERENCES

1. F.D. Chattaway, *J. Chem. Soc.*, **87**, 1884 (1905).
2. J.M. Bacchawat and N.C. Mathur, *Indian J. Chem.*, **9**, 1335 (1971).
3. M.U. Khan, J.K. Verma, V.R. Singh and H.P. Dwivedi, *Oxid. Commun.*, **16**, 235 (1993).
4. V.P. Singh, M.U. Khan and D.B.S. Chauhan, *Oxid. Commun.*, **20**, 124 (1997).
5. K. Vijaymohan, P. Raghunathrao and E.V. Sundaram, *Proc. Indian Acad. Sci.*, **58A**, 49 (1988).
6. M.U. Khan, P.K. Tiwari, J.K. Verma and H.D. Gupta, *Oxid. Commun.*, **20**, 117 (1997).
7. M.U. Khan, J.K. Verma, S.K. Nigam and S.S. Parihar, *Oxid. Commun.*, **21**, 362 (1998).
8. M.U. Khan, S.K. Nigam, J.K. Verma and A. Nigam, *Oxid. Commun.*, **18**, 304 (1995).
9. M.Z. Barkat and M.F. Abdel Wahab, *Anal. Chem.*, **26**, 1973 (1954).
10. A. Meenakshi and M.Santappa, *Indian J. Chem.*, **11**, 393 (1973).
11. J.S. Litter and W.A. Waters, *J. Chem. Soc.*, 827 (1962).
12. K.B. Wiberg and H. Schaefer, *J. Am. Chem. Soc.*, **91**, 933 (1969).
13. M.M. Mhala and K.J. Singh, *J. Indian Chem. Soc.*, **57**, 1076 (1989).
14. H.L. Riley, J.F. Moreley and N.A. Friend, *J. Chem. Soc.*, 1875 (1932).
15. S. Tiwari, M.U. Khan, B.M.L. Tiwari, K.S. Tiwari and N.D. Valechha, *Oxid. Commun.*, **22**, 416 (1999).

(*Received*: 8 July 2002; *Accepted*: 5 October 2002) AJC-2897