

Kinetics of Oxidation of 4-Oxo-4-phenylbutanoic Acid by N-Chlorosuccinimide in Aqueous Acetic Acid Medium

N.M.I. ALHAJI, N.A. MOHAMED FAROOK* and A.M. UDUMAN MOHIDEEN

Post-Graduate and Research Department of Chemistry, Khadir Mohideen College, Adirampattinam-614 701 (Thanjavur), India

E-mail: nafarook@msn.com web site: <http://farook.educations.net>

Oxidation of 4-oxo-4-phenylbutanoic acid (4-oxoacid) by N-chlorosuccinimide (NCS) has been investigated in 50% acetic acid-50% water (v/v) mixture. The reaction is first order each in [NCS] and [4-oxoacid]. An increase in rate is observed with increase in $[H^+]$. A decrease in the dielectric constant of the medium at constant concentration of other reactants has negligible effect on the rate of reaction. Variation in ionic strength of the medium and the addition of one of the reaction products (succinimide) has no significant effect on the rate of the reaction. From the kinetic data obtained at different temperatures, the activation parameters have been computed and a suitable mechanism has been proposed.

Key Words: Kinetic, 4-Oxo-4-phenylbutanoic acid, Oxidation, N-Chlorosuccinimide.

INTRODUCTION

The chemistry of reactions of N-halo compounds forms a separate branch, which is of great synthetic importance. N-halo compounds have been extensively employed as halogenating and oxidizing agents for organic substrates¹⁻¹³. Among the large variety of N-halo compounds extensively used as reagents in organic chemistry N-chloro compounds have received limited attention¹¹⁻¹³. N-chlorosuccinimide is a source of positive halogen and this reagent has been exploited as an oxidant for a variety of substrates¹¹⁻¹⁴ in both acidic and alkaline media. The nature of active oxidizing species and mechanism depend on the nature of the halogen atom, the groups attached to the nitrogen and the reaction conditions. We report herein the kinetics of oxidation of 4-oxo-4-phenylbutanoic acid (4-oxoacid) by N-chlorosuccinimide (NCS) in 50% acetic acid-50% water (v/v) mixture in the presence of perchloric acid. The progress of the reaction was followed potentiometrically.

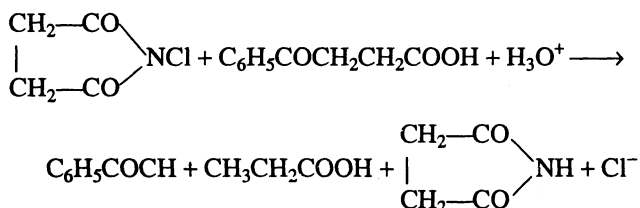
EXPERIMENTAL

4-Oxo-4-phenylbutanoic acid was prepared by the Friedel-Crafts acylation of benzene with succinic anhydride. All the chemicals used were of AR grade. Solutions of N-chlorosuccinimide (S.D. Fine) were prepared freshly and standard-

ized iodometrically. Acetic acid was distilled over chromic oxide before use. Perchloric acid was used as a source of hydrogen ions and sodium perchlorate was added to maintain the ionic strength constant. Double distilled water was employed in all the kinetic runs.

The kinetic studies were carried out under pseudo first order conditions. A large excess of 4-oxoacid was taken as compared to N-chlorosuccinimide concentration. The temperature of the reaction mixture was maintained with an accuracy of $\pm 0.1^\circ\text{C}$. The reaction was followed potentiometrically by setting up of the reaction mixture into which the platinum electrode and reference electrode (standard calomel electrode) were dipped. The emf of the cell was measured periodically using an Equip-Tronic potentiometer, while the reaction mixture was continuously stirred. The pseudo first-order rate constant (k_1) in each kinetic run was evaluated from the slope of the linear plot of $\log(E_t - E_a)$ against time (t) ($r > 0.995$). The second order rate constant (k_2) was obtained as $k_2 = k_1/[4\text{-oxoacid}]$.

The reaction mixture of 4-oxoacid and N-chlorosuccinimide at constant concentration of $[\text{H}^+]$ was allowed to remain together till the completion of the reaction and the product was found to be the corresponding benzoic acid and succinimide which was characterized by m.p. and their spot test. The results are in good agreement with 1 : 1 stoichiometry. The stoichiometry of the oxidation reaction may be represented by the following equation:



RESULTS AND DISCUSSION

The kinetics of oxidation of 4-oxo-4-phenylbutanoic acid follows first order with respect to oxidant under the condition $[\text{NCS}] \ll [4\text{-oxoacid}]$, which is evidenced by the linear plots of $\log(E_t - E_a)$ vs. time ($r > 0.988$) and also by constant values of the pseudo first-order rate constants at different $[\text{NCS}]$ at constant $[4\text{-oxoacid}]$ (Table-1). On varying $[4\text{-oxoacid}]$ at constant $[\text{NCS}]$ the second order rate constants gave almost constant values. These results indicate the first order dependence of the 4-oxoacid on the rate of the reaction. This is further supported by the fact that the plot of $\log k_1$ against $\log [4\text{-oxoacid}]$ is linear with a slope value of 1.003 ($r = 0.992$) and the plot of k_1 vs. $[4\text{-oxoacid}]$ gives a straight line passing through the origin ($r = 0.987$).

The kinetics of the oxidation have been studied in the presence and absence of hydrogen ions. In the absence of mineral acid, the reaction occurs very slowly. However, the reaction rate is enhanced remarkably when mineral acid is used as catalyst. The dependence of the reaction rate on the hydrogen ion concentration has been studied (Table-2). The rate of the reaction increases linearly with

increase in concentration of perchloric acid in the range 0.5–1.1 M at constant ionic strength. The plot of $\log k_1$ against $\log [H^+]$ is linear with a slope value of 1.01 ($r = 0.988$). This establishes that the reaction is first order with respect to hydrogen ion in the concentration range mentioned above.

TABLE-1
DEPENDENCE OF RATE ON [NCS] AND [4-OXOACID]

Solvent: 50% AcOH-50% H₂O (v/v) mixture, Temperature: 303 K

10^3 [NCS] (mol dm ⁻³)	10^2 [4-oxoacid] (mol dm ⁻³)	$10^4 k_1$ (s ⁻¹)	$10^3 k_2$ (dm ⁻³ mol ⁻¹ s ⁻¹)
2.0	2.0	1.41	7.05
2.0	3.0	2.12	7.06
2.0	4.0	2.85	7.12
2.0	6.0	4.24	7.06
2.0	8.0	5.68	7.11
3.0	0.2	1.42	7.10
4.0	0.2	1.44	7.21
6.0	0.2	1.45	7.25
8.0	0.2	1.41	7.05

TABLE-2
EFFECT OF VARYING $[H^+]$ AND $[NaClO_4]$
ON THE RATE OF REACTION

10^2 [4-oxoacid] = 2.0 mol dm⁻³, 10^3 [NCS] = 2.0 mol dm⁻³, temp. = 303 K

$[H^+]$ (mol dm ⁻³)	$NaClO_4$ (mol dm ⁻³)	$10^4 k_1$ (s ⁻¹)
0.5	0.5	1.41
0.7	0.5	1.95
0.9	0.5	2.55
1.1	0.5	3.12
0.5	0.8	1.45
0.5	1.32	1.39
0.5	1.4	1.38
0.5	1.6	1.42

The change in the polarity of the medium has a negligible effect on the reaction rate (Table-3). As acetic acid percentage is increased, the reaction rate increases very slowly. From the literature¹⁴ it is known that, as acetic acid percentage is increased three times, the reaction rate also increases by about three times. The trend observed in the rate constant values may be due to more than one factor. It

may be attributed to the lowering of dielectric constant of the medium which favours reactions involving protonation. Further, the enolization of the oxoacid may be catalyzed by acetic acid and this may also contribute to rate enhancement.

The observed negligible enhancement of the reaction rate with increase in the amount of acetic acid content at constant [perchloric acid] in the present study may be due to the less possibility of enolization and to the involvement of neutral species in the reaction.

The effect of ionic strength was studied by varying the concentration of sodium perchlorate in the reaction medium. The rate of oxidation is unaffected by change in ionic strength (Table-3). This may presumably be due to the attack of an ion on a neutral molecule in the rate determining step¹⁵.

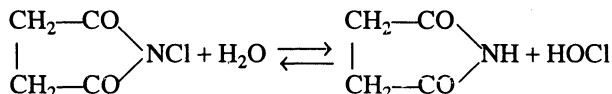
TABLE-3
EFFECT OF VARYING SOLVENT COMPOSITION
ON THE RATE OF OXIDATION

10^2 [4-oxoacid] = 2.0 mol dm⁻³, 10^3 [NCS] = 2.0 mol dm⁻³,
Temperature = 303 K

D	AcOH-H ₂ O (v/v %)	$10^4 k_1$ (s ⁻¹)
37.50	50-50	1.41
34.75	55-45	1.49
31.50	60-40	1.57
28.50	65-35	1.65
25.90	70-30	1.71

The reaction mixture was kept for 24 h with acrylonitrile in an inert atmosphere. Test for free radical was negative. This clearly establishes the absence of free radical formation during the NCS oxidation of 4-oxoacid. The rate of reaction was measured at different temperatures. The enthalpy and entropy of activation were calculated. The value of entropy of activation is supportive of C—C bond cleavage in the substrate leading to the formation of benzoic acid.

It is known¹² that the probable reactive species of NCS in acid solution are >NCl, HOCl, >N⁺HCl, H₂O⁺Cl. The retardation of reaction on the addition of succinimide suggests a pre-equilibrium (see eqn.) in which succinimide is one of the products.

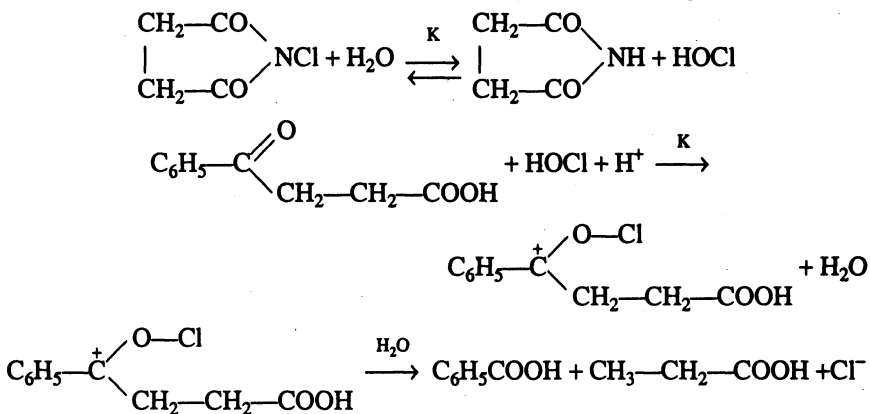


In the oxidation process HOCl is the reactive oxidizing species. In solution containing acetic acid, one cannot exclude the possibility of (OAc—HCl) acting as a reactive oxidizing species. The observed negligible enhancement of the reaction rate with increase in amount of acetic acid content at constant [perchloric acid] might be due to involvement of neutral species in the reaction. If the reaction were to be catalyzed by acetate ions there should not have been a large increase in rate with increase in acetic acid content of the medium. Hence catalysis by acetate ion is untenable.

To account for the unusual dependence of reaction rate on [H⁺], [HOCl] formed

in a rate limiting hydrolysis of molecular NCS which in aqueous medium due to its positive chlorine end is likely to associate with one water molecule, is proposed to react with the substrate in a fast step.

Based on the above discussion, the following mechanism is possible:



Based on the proposed mechanism, the rate law for the NCS oxidation of 4-oxoacid in protic solvent may be written as:

$$\frac{-d[\text{NCS}]}{dt} = kK[\text{oxoacid}][\text{NCS}][\text{H}^+]$$

The proposed mechanism and rate law are in conformity with the observed experimental features.

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