THE KINETICS OF OXIDATION OF SECONDARY ALCOHOLS BY N-CHLOROSUCCINIMIDE

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N-halogeno compounds in general and N-chlorosuccinimide (NCS) in particular are known to oxidise primary and secondary alcohols smoothly and quantitatively to the corresponding carbonyl compounds[1]. While it is generally accepted that with these oxidants a 'positive' halogen is the attacking species in polar media, the kinetics and mechanism of these reactions have not been elucidated. In   recent kinetic studies on N-bromosuccinimide (NBS) oxidation of alcohols[2,3], it was shown that the oxidation proceeds in two stages, first by a slow reaction with NBS, followed by a rapid reaction with molecular bromine. Further, it was demonstrated that the incursion of bromine oxidation can be suppressed completely by the addition of Hg(II) salts.

We report in this communication, our observations on the differential kinetic behaviour of the analogous compound, NCS in the oxidation of secondary alcohols. The experiments were carried out under conditions where photochemical reactions could be excluded. The kinetics were followed by estimating the unreacted NCS at various time intervals by an iodometric procedure[2]. The reaction is characterised by an induction period. After a sluggish period varying between 5 - 15 minutes, the reaction exhibits a smooth first order dependence on NCS. But the most interesting aspect of this work is that the rate of oxidation exhibits a zero order dependence on alcohol and is found to increase with increase in the concentration of added chloride ions. The induction period is also considerably reduced by the added chloride ion. At low acidity (0.1M $HClO_4$), the plot of log k_1 versus log $[Cl^-]$ is linear with a slope of 0.75. On the otherhand, a 'double-reciprocal' plot of $1/k_1$ versus

$1/[Cl^-]$ is linear with a definite Y-intercept, apparently following Michaelis-
Menton kinetics. However, at higher acidities viz., 0.2M and 0.3M $HClO_4$, a clean
first order dependence on $[Cl^-]$ over the concentration range 0.2M-0.5M is observed
(Table 1). Surprisingly, unlike NBS oxidation, the rate is invariant with the
concentration and nature of the alcohol both in the presence and the absence of
added halide ion (Table 2).

TABLE 1

Effect of added chloride ion

$[Propan-2-ol]$ = 0.023M $[NCS]$ = 0.002M   Solvent: 100% H_2O

[NaCl]	$k_1 \times 10^5$ sec^{-1} at 55°C		
(M)	0.1M $HClO_4$	0.2M $HClO_4$	0.3M $HClO_4$
0.02	2.38	2.20	2.56
0.03	3.20	3.39	3.84
0.04	4.04	..	..
0.05	4.42	5.80	6.66
0.06	4.52	..	..

TABLE 2

Dependence of rate on the concentration and the nature of alcohol

$[HClO_4]$ = 0.1M $[NaCl]$ = 0.05M   Temp. 55°C

ALCOHOL	$[Alcohol]$ M	Solvent composition (% v/v) ButOH – H_2O	$k_1 \times 10^5$ sec^{-1}
Propan-2-ol	0.01166	0 – 100	4.39
	0.02332	0 – 100	4.42
	0.03498	0 – 100	4.39
	0.04664	0 – 100	4.39
Butan-2-ol	0.02350	0 – 100	4.30
	0.03240	0 – 100	4.32
Pentan-2-ol	0.02315	0 – 100	4.40
	0.03146	0 – 100	4.38
Propan-2-ol	0.02250	20 – 80	23.1
Butan-2-ol	0.02196	20 – 80	23.1
1-Phenyl ethanol	0.02095	20 – 80	23.0
Cyclohexanol	0.02216	20 – 80	23.1

These observations lead us to the view that, in the presence of Cl⁻, the rate of the reaction is governed by the rate of interaction between the protonated NCS and Cl⁻ to produce a steady small concentration of chlorine which is consumed by the alcohol in a rapid stage.

$$NCSH^+ \; + \; Cl^- \; \underset{\xrightarrow{\hspace{1cm}}}{\overset{slow}{\xleftarrow{\hspace{1cm}}}} \; Cl_2 \; + \; SH \qquad (i)$$

$$Alcohol \; + \; Cl_2 \; \xrightarrow{fast} \; Products \qquad (ii)$$

Oxidation by NBS in presence of Br⁻ is essentially oxidation by bromine[2] with the corresponding step (i) fast and step (ii) as the rate-determining one, thereby leading to a dependence of rate on the concentration of the alcohol. Oxidation by NCS in presence of Cl⁻ though conceived as passing through molecular chlorine differs significantly with step (i) as rate-determining, leading to a zero order dependence on the alcohol concentration.

A relevant comparison to this behaviour of NCS is the transformation of N-chloroacetanilide into ortho and para chloroacetanilides (Orton rearrangement[4]) wherein the rate-determining step is the interaction between HCl and the chloramine to produce chlorine followed by a rapid reaction between chlorine and acetanilide. More significantly, the transformation in presence of chlorine consumers like phenol, p-cresol and acetanilide has the same rate and is unaffected by the amount of the substrate[5,6], thus paralleling the NCS oxidation of alcohols.

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