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Oxidation of Cyclopentanone by N-Chlorosuccinimide in Presence of Rhodium(III) Chloride as Catalyst in Acidic Medium

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Kinetic studies on oxidation of cyclopentanone by N-chlorosuccinimide reagent in presnece of rhodium(III) chloride as catalyst in acidic medium have been studied to obtain the order of reaction with respect to N-chlorosuccinimide.

Key Words: Cyclopentanone, N-Chlorosuccinimide, Rhodium(III) chloride.

INTRODUCTION

Cyclopentanones are important biologically active compounds. N-Chlorosuccinimide is a versatile halogenating agent especially for allylic halogenation and has been found to be more stable than N-bromosuccinimide or N-bromoacetamide[1-3]. N-Chlorosuccinimide has been used for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively. Kinetic studies of secondary alcohols by N-chlorosuccinimide has been reported by Srinivasan *et al.*[4]. They have also studied the difference between oxidation capabilities of N-bromosuccinimide and N-chlorosuccinimide.

Sharma *et al.*[5] studied the reaction of N-chlorosuccinimide with indoles and found it to be a very important reagent for the derermination of indole derivatives. The oxidation of various substrates were also studied in presence of a number of catalysts *e.g.*, Cu(II)[6], Ag(I)[7], Cr(III)[8], Mn(II)[9], Os(VIII)[10-14], ruthenium(III) chloride[12-18] and Rh(IV) chloride[19].

Kinetics and mechanism of Rh(III) catalyzed oxidation of 1,2-glycols by acid bromate have been reported[20]. Kinetics and mechanism of Rh(III) catalyzed oxidation of polyhydric alcohols by acidified potassium bromate have been reported[21]. Equilenin acetate and dehydro equilenin acetate were oxidized with iodosobenzene and rhodium(III) catalyst. The selectivity of reactions differs from that with the corresponding Mn(II) catalyst or from that of free radical chain oxidation[22]. The rate determining step in the rhodium-xantphos catalyzed hydroformylation of 1-octene has been reported[23].

EXPERIMENTAL

All the reagents were of highest purity. The reaction vessels as well as the storage vessels containing reagents were coated black from outside to prevent any photochemical degradation. Jena glass stills were used. A NAINA electronic digital pH meter was used for pH measurements.

Aqueous solution of butanone was prepared by dissolving the calculated volume of the substance in known volume of water acidified with acetic acid. A pure sample of N-chlorosuccinimide (NCS) was used for the research work by dissolving the requisite amount in known volume of double distilled water rhodium(III) chloride (Johnson Mathey) solution in double distilled water was used for catalytic purpose.

Appropriate weight of sodium thiosulphate (AR, BDH) was dissolved in water and a pinch of sodium carbonate (AR, BDH) was added to it and the resultant solution was standardized against copper sulphate solution by iodometric method. Sodium perchlorate (AR Riedel) 4 % potassium iodide (AR, BDH), potassium chloride (AnalaR, BDH) solutions were prepared by dissolving appropriate weight of the samples in double distilled air free water methanol (AnalaR, BDM) was used as such.

Procedure: Reaction mixture containing requisite amount of the substrate, acetic acid, rhodium(III) chloride and water were allowed to equilibrate for about 0.5 h in a thermostat maintained at a desired temperature within ± 0.1 ºC range. The NCS solution was brought to the same temperature by placing the vessel in the same thermostat for 0.5 h. Appropriate volume of N-chlorosuccinamide was added to the reaction mixture to initiate the reaction by vigorous shaking for some time.

The total initial volume of the reaction mixture was always kept at 50 mL in each case 5 mL aliquot portions of the reaction mixtures were withdrawn at appropriate time intervals and quickly transferred to a titration flask containing 5 mL of 4 % potassium iodide solution. Unreacted NCS liberated an equivalent amount of iodine from acidified potassium iodide solution which was titrated against standard sodium thiosulphate solution using fresh starch solution as indicator.

RESULTS AND DISCUSSION

In order to obtain the dependence of the rate on the NCS and thereby to obtain the order of reaction with respect to NCS, a series of kinetic measurements were made by taking different initial concentration of NCS separately with cyclopentanone. Keeping other parameters constant. The results of there studies at two different temperatures (30 and 35 °C) are presented in Tables 1-3.

The reaction rate was found to be of first order with respect to NCS by calculation as well as graphical measurements [plot of log(a-x) against time (Figs. 1 and 2) being straight lines with different concentrations of N-chlorosuccinimide.

TABLE-1
RATE OF OXIDATION OF CYCLOPENTANONE BY NCS AT DIFFERENT INITIAL CONCENTRATION OF N-CHLOROSUCCINIMIDE (NCS) AT 30 ºC
Cyclopentanone – 1 × 10^{-2} M, [Rh(III) = 0.88 × 10^{-6} M, pH = 2.58, [CI^{-1}] = 3.6 × 10^{-3} M

Time (min)	NCS × 10^3 M				
	0.6 Hypo (mL)	0.8 Hypo (mL)	1.0 Hypo (mL)	1.2 Hypo (mL)	1.4 Hypo (mL)
0	3.71	4.97	6.15	7.40	8.67
10	3.41	4.20	5.13	6.25	7.23
20	2.71	3.63	4.46	5.37	6.19
30	2.29	3.11	3.82	4.63	5.47
45	1.81	2.46	3.05	3.63	4.25
60	1.51	2.02	2.50	3.08	3.51
75	1.12	1.50	1.84	2.23	2.67
90	0.87	1.18	1.42	1.77	2.03
100	0.70	0.95	1.18	1.41	1.67
120	0.56	0.70	0.91	1.10	1.33
K_1 × l0^4 s^{-1}	2.60	2.64	2.70	2.62	2.74

TABLE-2
RATE OF OXIDATION OF CYCLOPENTANONE BY NCS AT DIFFERENT INITIAL CONCENTRATIONS OF N-CHLOROSUCCINIMIDE (NCS) AT 35 ºC
Cyclopentanone - 1.0 × 10^{-2} M, [Rh(III) = 0.88 × 10^{-6} M, pH = 2.58, [Cl^{-1}] = 3.6 × 10^{-3} M

Time (min)	NCS × 10^3 M				
	0.6 Hypo (mL)	0.8 Hypo (mL)	1.0 Hypo (mL)	1.2 Hypo (mL)	1.4 Hypo (mL)
0	3.70	4.97	6.15	7.43	8.71
10	2.87	3.83	4.69	5.80	6.57
20	2.21	2.97	3.63	4.40	5.00
30	1.77	2.37	2.89	3.35	4.11
45	1.19	1.59	1.97	2.31	2.71
60	0.83	1.13	1.39	1.69	1.91
75	0.50	0.67	0.83	0.91	1.17
90	0.30	0.50	0.63	0.75	0.88
105	0.24	0.33	0.39	0.45	0.58
120	0.12	0.19	0.21	0.23	0.25
K_1 × 10^4 s^{-1}	4.30	4.31	4.38	4.44	4.40

TABLE-3
VALUES OF FIRST ORDER RATE CONSTANTS AT DIFFERENT CONCENTRATION OF N-CHLOROSUCCINIMIDE (NCS). K × l0^4 s^{-1}

Initial NCS × 10^3 M	Cyclopentanone	
	30 ºC	35 ºC
0.6	2.58	4.28
0.8	2.62	4.29
1.0	2.55	4.36
1.2	2.60	4.41
1.4	2.70	4.43
Average	2.65	4.37

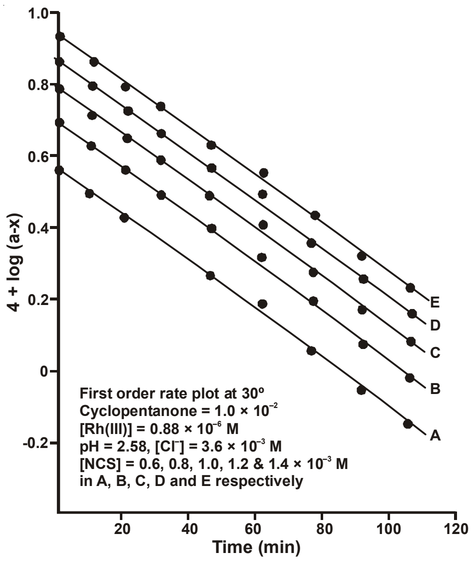

Fig. 1

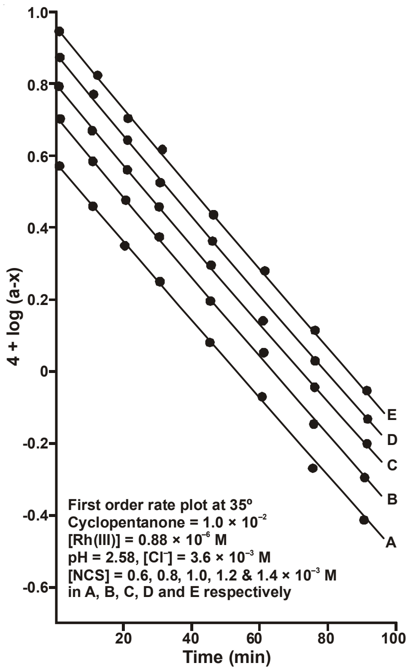

Fig. 2

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