Oxidation of Borneol and Isoborneol by Pyridinium Chlorochromate and 4,4'-(*N,N*-Dimethylamino)pyridinium Chlorochromate-A Kinetic Study†

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Oxidation of alcohols by a variety of oxidizing agents has attracted the attention of numerous workers owing to the commercial value of products. Extensive kinetic studies have been made on the oxidation of several organic substrates by oxidants like pyridinium chlorochromate, imidazolium dichromate, quinolinium chlorochromate and quinolinium fluorochromate by earlier workers. However, there are no reports so far on the kinetics of oxidation of bicyclic secondary alcohols with pyridinium chlorochromate and 4,4'-(*N,N*-dimethylamino)pyridinium chlorochromate (DMAPCC) which are mild efficient and practical reagents for oxidation reactions. In this present work pyridinium chlorochromate and DMAPCC were synthesized and purified. The results of the kinetics of the oxidation of borneol and isoborneol with pyridinium chlorochromate and DMAPCC in aqueous DMF (50 % v/v) medium in the presence of perchloric acid is reported. This current research work proposes the mechanism based on kinetics of oxidation of borneol and isoborneol. The kinetics of oxidation of borneol and isoborneol by pyridinium chlorochromate and 4-(*N,N*-dimethylamino) pyridinium chlorochromate in 50 % dimethylformamide solution was investigated. The influence of substrate, temperature, acid strength on the kinetics of the reaction and substrate in order of reaction was studied. The activation parameters such as $\Delta G^{\pm}$, $\Delta H^{\pm}$ and $\Delta S^{\pm}$ were also determined.

Key Words: Borneol, Pyridinium chlorochromate, 4,4'-(*N,N*-Dimethylamino)pyridinium chlorochromate, Isoborneol, Kinetics.

INTRODUCTION

Oxidation of alcohols by a variety of oxidizing agents has attracted the attention of numerous workers[1,2]. The development of new techniques and procedure reported[3,4] for chromium oxidation continues to be the topic of current interest for organic chemists. Recently a number of new chromium(VI) reagent with special reaction conditions have been developed for the chromospecific, regiospecific and stereospecific oxidation of various functional groups[5-9]. These oxidizing agents are soluble in water and variety of organic solvents. The usage of minimum amount of oxidant and easybhandling makes these oxidizing agent more advantageous. This prompted us to embark on the kinetics of oxidation of several cyclic and acyclic organic substrates by pyridinium chlorochromate (PCC), 4-(*N,N*-dimethylamino)pyridinium chlorochromate (DMAPCC). However, there are no reports so far on the kinetics of oxidation of bicyclic secondary alcohols with pyridinium chlorochromate, DMAPCC and quinolium chlorochromate, which are mild, efficient and practical reagents for oxidation reactions. In this present study the results of the kinetics of the oxidation of borneol and isoborneol with pyridinium chlorochromate and DMAPCC in aqueous DMF (50 % v/v) medium in the presence of perchloric acid are reported and discussed.

EXPERIMENTAL

All the chemicals used were of Analar grade Borneol and Isoborneol were procured from Fluka, Puris.

Preparation of DMF: AR grade dimethylformamide was further purified by the reported method[10]. Aqueous DMF (ie) 40, 50, 60, 70 and 80 % (v/v) were prepared by mixing appropriate volumes of double distilled water and DMF purity of DMF. The dielectric constant values for various DMF-H_2O solution were measured by open-ended coaxial probe technique at microwave frequency using HP8720 A network analyzer.

Preparation of pyridinium chlorochromate: Pyridinium chlorochromate was prepared by following the procedure given by Agarwal *et al.*[7]. To 100 g CrO_3 about 184 mL of 6 M HCl was added in RB flask with constant stirring. The homogenous solution was cooled to 0 ºC and 79.1 g pyridine was added. The orange solid obtained was recooled to 0 ºC and dried in vacuum.

Preparation of 4-(*N,N*'-dimethylamino) pyridinium chlorochromate: 4 g of 4-(*N,N*'-dimethylamino) pyridinium

chlorochromate was added to ice-cold solution of chromium trioxide (3.27 g) in 20 mL of aqueous hydrochloric acid with vigorous stirring for 0.5 h. Yellow -orange solid was obtained and dried under vacuum.

Purity of pyridinium chlorochromate and DAMPCC was estimated by iodometric method: The kinetics of reaction was followed by estimating the unreacted oxidant. The reaction was carried out under pseudo-first order condition ([S] >> [OX]) at constant temperature in an electrically operated thermostat (± 1 °C). The unreacted oxidant was estimated iodometrically by titrating against standardized sodium thiosulphate. The stoichiometry of the reaction between the reactants borneol,isoborneol and the oxidants pyridinium chlorochromate, DMAPCC was determined under kinetic concentration and found to be 1:1.

Product analysis: The product obtained was quantitatively identified by TLC technique and it was analyzed by FT-IR and NMR spectral analysis.

RESULTS AND DISCUSSION

Effect of variation of substrate on kinetics of reaction: The kinetics of oxidation of bicyclic secondary alcohols *viz.*, borneol and isoborneol by pyridinium chlorochromate studied in aqueous dimethylformamide (50 % v/v) medium in the presence of perchloric acid at 303 K. The results are summarized in Table-1 (Fig. 1).

TABLE-1
EFFECT OF VARIATION OF SUBSTRATE ON OXIDATION
OF BORNEOL AND ISOBORNEOL BY PCC

$[S] \times 10^3$/mol dm^{-3}	$3 + \log [S]$	Borneol		Isoborneol	
		$k_1 \times 10^4$/s^{-1}	$4 + \log k_1$	$k_1 \times 10^4$/s^{-1}	$4 + \log k_1$
07.5	0.8751	3.34	0.5238	04.53	0.6561
10.0	1.0000	4.97	0.6911	06.59	0.8189
12.5	1.0969	5.93	0.7731	07.95	0.9004
15.0	1.1761	6.93	0.8407	09.07	0.9576
17.5	1.2430	8.24	0.9159	11.11	1.0457

(Reaction conditions: PCC = 1×10^{-3} mol dm^{-3}, DMF-H$_2$O = 50 % (v/v), HClO$_4$ – 2×10^{-1} mol dm^{-3} and temperature = 303 K)
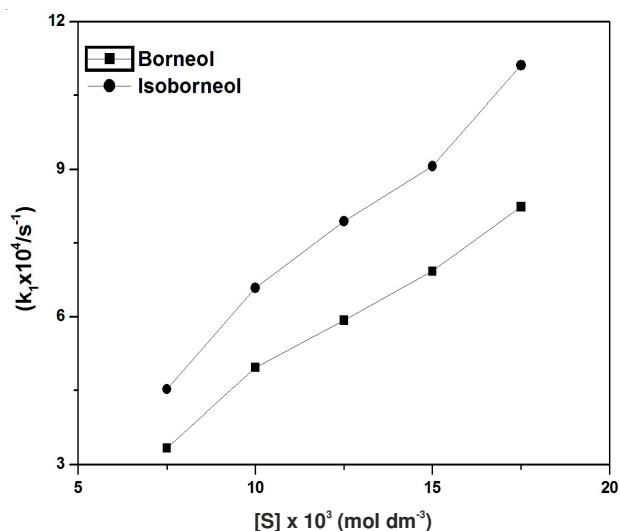

Fig. 1. Order of reaction in oxidation of Borneol and Isoborneol by pyridinium chlorochromate and DMAPCC

The kinetics of oxidation of bicyclic secondary alcohols *viz.*, borneol and isoborneol by DMAPCC studied in aqueous dimethylformamide (50 % v/v) medium in the presence of perchloric acid at 303 K. The results are summarized in Table-2 (Fig. 2).

TABLE-2
EFFECT OF VARIATION OF SUBSTRATE ON OXIDATION
OF BORNEOL AND ISOBORNEOL by DMAPCC

$[S] \times 10^3$/ mol dm^{-3}	$3 + \log [S]$	Borneol		Isoborneol	
		$k_1 \times 10^4$/ s^{-1}	$4 + \log k_1$	$k_1 \times 10^4$/ s^{-1}	$4 + \log k_1$
07.5	0.8751	3.18	0.5024	3.75	0.5740
10.0	1.0000	4.01	0.6031	5.25	0.7202
12.5	1.0969	5.14	0.7110	6.25	0.7959
15.0	1.1761	6.22	0.7938	7.58	0.8797
17.5	1.2430	7.10	0.8513	9.36	0.9713

(Reaction conditions: DMAPCC = 1×10^{-3} mol dm^{-3}, DMF-H$_2$O = 50%(v/v); HClO$_4$ – 2×10^{-1} mol dm^{-3} and temperature = 303 K)
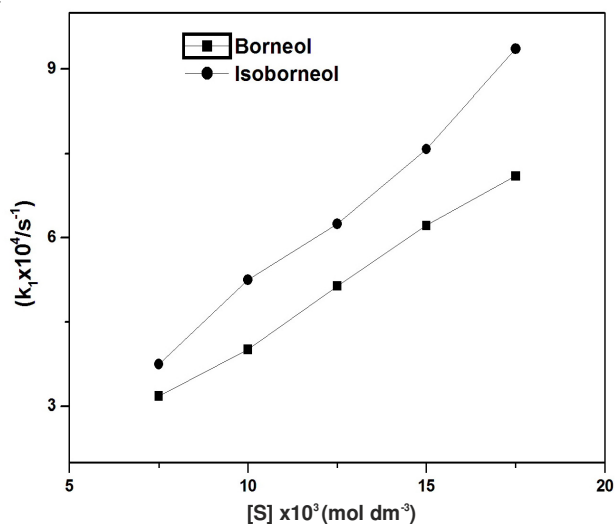

Fig. 2. Order of reaction in oxidation of Borneol and Isoborneol by pyridinium chlorochromate and DMAPCC

The order with respect to the substrate was measured by changing the [Sub] and keeping the [OX], [H$^+$] and temperature constant. The slope of linear plot of log K$_{obs}$ *versus* log[S] was found to be unity and plot of K$_{obs}$ *versus* [S] was linear passing through the origin indicating a first order dependence on [Substrate].

Effect of variation of oxidant on order of reaction: The results obtained for order of the reaction for oxidation of bicyclic secondary alcohols *viz.*, borneol and isoborneol by pyridinium chlorochromate and DMAPCC studied in aqueous dimethylformamide (50 % v/v) medium in presence of the perchloric acid at 303 K (Table-3).

Effect of variation of acid strength on oxidation of borneol and isoborneol: The results obtained for order of the reaction for oxidation of bicyclic secondary alcohols *viz.*, borneol and isoborneol by pyridinium chlorochromate and DMAPCC studied in aqueous dimethylformamide (50 % v/v) medium in the presence of perchloric acid at 303 K are summarized in Table-4 (Figs. 3 and 4).

TABLE-3
OXIDATION OF BORNEOL AND ISOBORNEOL
BY PCC AND DMAPCC

Oxidants	Concentration	Borneol ($k_1 \times 10^4/s^{-1}$)	Isoborneol ($k_1 \times 10^4/s^{-1}$)
[PCC] $\times 10^4$ /mol dm^{-3}	07.5	4.97	6.596
	10.0	4.96	6.59
	12.5	4.96	6.59
	15.0	4.99	6.40
	17.5	4.93	6.59
[DMAPCC] $\times$ 10^3 /mol dm^{-3}	07.5	4.05	5.29
	10.0	4.03	5.26
	12.5	4.07	5.25
	15.0	4.04	5.23
	17.5	4.05	5.25

(Reaction conditions: [S] = 1×10^{-2} mol dm^{-3}, DMF-H$_2$O = 50 % (v/v), HClO$_4$ – 2×10^{-1} mol dm^{-3} and temperature = 303 K)

Increase of perchloric acid concentration from 0.15 to 0.35 M enhanced the rate of oxidation (Table-4). The plots of log k_2 *versus* log[[H$^+$] indicate impressive linear relationship but the slopes were far less than unity.

Effect of temperature on oxidation of borneol and isoborneol: The reaction was studied at various temperatures to evaluate activation parameters. The pseudo first order rate constant at different temperatures are given in Figs. 5 and 6 and the values are tabulated in Table-5. The thermodynamic parameters are tabulated in Table-6.
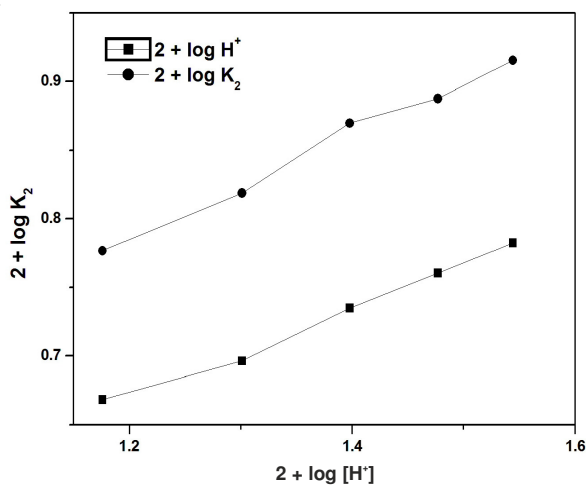

Fig. 3.   Acid strength on oxidation of borneol and isoborneol by PCC and DMAPCC
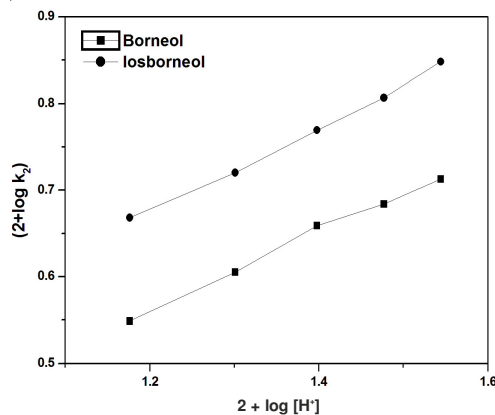

Fig. 4.   Acid strength on oxidation of borneol and isoborneol by PCC and DMAPCC
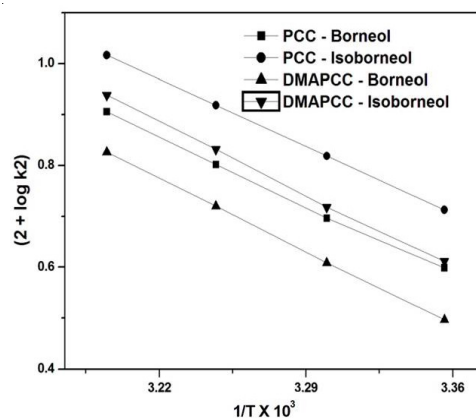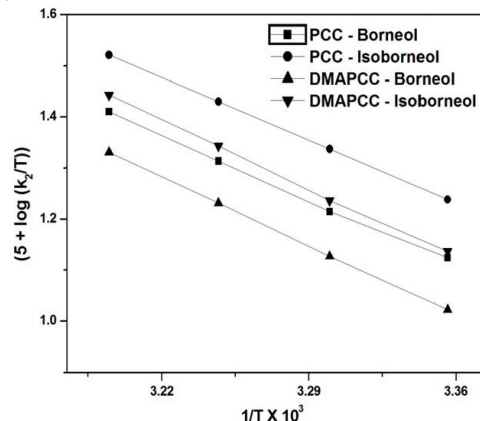

Fig. 5. Arrhenius and Laidler-Eyring plot

Fig. 6. Arrhenius and Laidler-Eyring plot

TABLE-4
EFFECT OF ACID STRENGTH ON OXIDATION OF BORNEOL AND ISOBORNEOL

Oxidants	HClO$_4$/mol dm^{-3}	2+log [H$^+$]	Borneol			Isoborneol		
			$k_1 \times 10^4/s^{-1}$	$k_2 \times 10^3/dm^3\,mol^{-1}\,s^{-1}$	2 + log k_2	$k_1 \times 10^4/s^{-1}$	$k_2 \times 10^3/\,dm^3\,mol^{-1}\,s^{-1}$	2 + log k_2
PCC	0.15	1.1761	4.66	46.6	0.6684	5.98	59.8	0.7767
	0.20	1.3010	4.97	49.7	0.6964	6.59	65.9	0.8189
	0.25	1.3979	5.43	54.3	0.7348	7.41	74.1	0.8698
	0.30	1.4771	5.76	57.6	0.7604	7.72	77.2	0.8876
	0.35	1.5441	6.06	60.6	0.7825	8.23	82.3	0.9154
DMAPCC	0.15	1.1761	3.54	35.4	0.5490	4.66	46.6	0.6684
	0.20	1.3010	4.03	40.3	0.6053	5.25	52.5	0.7202
	0.25	1.3979	4.56	45.6	0.6590	5.88	58.8	0.7694
	0.30	1.4771	4.83	48.3	0.6840	6.41	64.1	0.8069
	0.35	1.5441	5.16	51.6	0.7127	7.05	70.5	0.8482

(Reaction conditions: [S] = 1×10^{-2} mol dm^{-3}, DMF-H$_2$O = 50 % (v/v), PCC and DMAPCC–1×10^{-3} mol dm^{-3} and temperature = 303 K)

TABLE-5
EFFECT OF TEMPERATURE ON OXIDATION OF BORNEOL AND ISOBORNEOL

Oxidants	T (K)	$1/T \times 10^3$	Borneol			Isoborneol		
			$k_1 \times 10^4/s^{-1}$	$2 + \log k_2$	$5 + \log (k_2/T)$	$k_1 \times 10^4/s^{-1}$	$2 + \log k_2$	$5 + \log (k_2/T)$
PCC	298	3.356	3.97	0.5988	1.1246	05.16	0.7127	1.2385
	303	3.300	4.97	0.6964	1.2149	06.59	0.8189	1.3374
	308	3.247	6.34	0.8021	1.3136	08.29	0.9186	1.4301
	313	3.195	8.05	0.9058112	1.4103	10.39	1.0165	1.5211
DMAPCC	298	3.356	3.14	0.4969	1.0227	4.09	0.6117	1.1369
	303	3.300	4.06	0.6085	1.1270	5.22	0.7177	1.2362
	308	3.247	5.25	0.7202	1.2317	6.79	0.8319	1.3434
	313	3.195	6.70	0.8261	1.3306	8.68	0.9385	1.4430

(Reaction conditions: [S] = 1×10^{-2} mol dm^{-3}, DMF-H$_2$O = 50 % (v/v), PCC and DMAPCC – 1×10^{-3} mol dm^{-3} and HClO$_4$ – 2×10^{-1} mol dm^{-3})

The activation parameters such as $\Delta G^\pm$, $\Delta H^\pm$ and $\Delta S^\pm$ calculated from temperature studies is given in Table-6.

TABLE-6
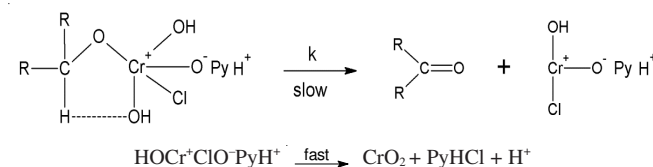ACTIVATION PARAMETERS CALCULATED FROM
TEMPERATURE STUDIES

Oxidant	Borneol				
	A (mol dm^{-3}s^{-1})	E_a (kJ mol^{-1})	$\Delta H^\pm$ (kJ mol^{-1})	$\Delta S^\pm$ (JK^{-1} mol^{-1})	$\Delta G^\pm$ (kJ mol^{-1})
PCC	1.05×10^5	36.66	34.13	-157.38	82.21
DMAPCC	2.39×10^5	39.27	36.74	-150.52	82.72
	Isoborneol				
PCC	1.11×10^5	36.14	33.60	-156.88	81.53
DMAPCC	2.82×10^5	39.09	36.63	-148.75	82.08

The mechanism of reaction is proposed as follows:

Mechanism and rate law
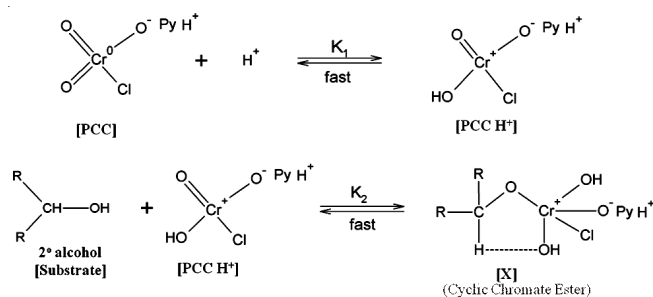
The formation of chromate ester assumed to be fast and the subsequent decomposition of the ester was the rate controlling step.

From the formula given below the rate of reaction was calculated.

$$\text{Rate} = k\ K_1 K_2\ [S]\ [A]_0\ [H^+]$$

The activation parameters for the oxidation of borneol and isoborneol are in good agreement with the mechanism proposed by us. The negative value of $\Delta S^\pm$ show that the cyclic transition state are more polar than the reactants.

Conclusion

In the Cr(VI) oxidation of bicyclic system of the pair borneol and isoborneol, the relative rates of oxidation indicate the isoborneol reacts faster than borneol because the chromate ester of isoborneol is sterically crowded and is oxidized faster.

The relative reactivity of pyridinium chlorochromate towards the oxidation of chosen epimeric bicyclic alcohols was found to be greater than 4,4'-(*N,N*-dimethylamino)pyridinium chlorochromate (DMAPCC).

PCC > DMAPCC

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