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A Comparative Study on the Kinetics of Oxidation of Some Secondary Alcohols By 1-Chloroben otriazole and Pyridinium Dichromate†

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The rates of reaction of 2-propanol (PRL), phenyl methyl carbinol (PMC) and diphenylcarbinol (DPC) with the oxidants, 1-chlorobenzotriazole (CBT) and pyridinium dichromate have been measured at 308, 313 and 318 K in acetic acid-water mixtures. In both the cases of study the order of the reaction is found to be one each with respect to oxidant and substrate and decreases of dielectric constant favours the rate, while variation of ironic strength and H^+ shows dissimilar observation. Suitable mechanisms and rate laws have been proposed for both the cases. An attempt has been made to explain the order of reactivity of this group of alcohols in the light of observed effects. The order of reactivity DPC > PMC > PRL is explained in the light of combined electron releasing effect and the steric strain.

INTRODUCTION

A great variety of new chromium (VI) oxidants[1–8] together with special reaction conditions have been introduced for the chemospecific, regiospecific and stereospecific oxidative degeneration of functional groups in highly sensitive systems. The exact form of chromium (VI) in acetic acid is still under discussion; it may well be in the form of dimers, trimers or large units[9]. Kinetics of oxidation of several substrates by PDC in our laboratories[10–12] gave a good idea that anhydrous conditions are more conductive to complexation of substrate with Cr(VI) and hence to mild oxidation. The advantage to use CBT, due to the simplicity of its preparation, kind of stability and the adjustability of conditions under which it can be employed both as a mild and vigorous oxidant have been experienced well in our previous findings[13–18]. The use of these two oxidants towards these secondary alcohols has not been made earlier.

EXPERIMENTAL

PDC and CBT were prepared respectively by known procedures[19,20] Then purities were determined by iodometric assay.

BDH samples of propan-2-ol and phenyl methyl carbinol were used

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TABLE 1

RATE DATA ON THE OXIDATION OF PRC WITH CBT AND PDC AT TEMPERATURE —308K

Sl. N.	[PRL] $\times 10^2$M	[PDC] $\times 10^4$M	[CBT] $\times 10^4$M	%AcOH–H_2O (v/v)	[$NaClO_4$] $\times 10^2$M	[$MnSO_4$] $\times 10^4$M	[KCl] $\times 10^2$M	[$HClO_4$] $\times 10^2$M	$k_{obs} \times 10^4$ sec.	$k_2 \times 10^2$M sec.
1.	4.21	5.01–15.03	—	90	—	—	—	—	6.04–3.39	—
2.	3.17–7.37	10.02	—	90	—	—	—	—	3.42–8.07	1.08
3.	4.21	10.02	—	75–90	—	—	—	—	0.76–8.29	—
4.	4.21	10.02	—	90	2.78–5.56	—	—	—	3.70–3.97	—
5.	4.80	10.30	—	90	—	0–9.96	—	—	1.99–0.99	—
6.	7.5–17.5	—	100.0	60	—	—	8.0	—	2.92–6.68	3.84
7.	10.0	—	70–110	60	—	—	8.0	—	4.13–4.19	—
8.	10.0	—	100.00	20–70	—	—	8.0	—	0.56–8.46	—
9.	10.0	—	100.00	60	—	—	5–14	—	3.74–7.37	—
10.	10.0	—	100.00	60	—	—	8.0	2–3.2	7.39–10.64	—

as such. Benzhydrol was prepared according to organic synthesis[21]. Other reagents used were of analytical grade. In both the cases the experiment was carried out by mixing the substrate and oxidant solution under pseudo first order conditions (always substrate in excess) in requisite quantity of aqueous acetic acid. The rate was followed iodometrically.

Product analysis under kinetic conditions gave only ketones in each case, identified as their 2,4-dinitrophenyl hydrazone derivatives and also with I.R. absorption at 1720 cm^{-1}.

Stoichiometry procedure should, all these alcohols observed a reaction of 1 : 1 stoichiometry in each case of study.

RESULTS AND DISCUSSION

The rate constants for the reaction of these secondary alcohols with the oxidants CBT and PDC are given in Table 1. The change in the experimental conditions are also incorporated in the same table. The relevant thermodynamic parameters are shown in Table 2.

TABLE 2

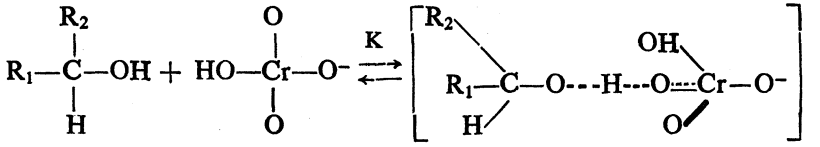
	CBT Oxidation Solvent : CH_3COOH-H_2O 60% (v/v) Temperature–308K			PDC Oxidation Solvent : CH_3COOH-H_2O 80% (v/v) Temperature–308K		
	$k_2 \times 10^{-3}$ 1 mol^{-1} sec^{-1}	$\Delta H^{\ddagger}$ KJmol^{-1}	$-\Delta S^{\ddagger}$ JKmol^{1}	$k_2 \times 10^{-3}$ 1 mol^{-1} sec^{-1}	$\Delta H^{\ddagger}$ KJmol^{-1}	$-\Delta S^{\ddagger}$ JKmol^{-1}
PRL	3.84	87.18	5.33	3.54	45.69	134.45
PMC	11.2	66.03	66.72	22.8	37.81	154.07
DPC	11.4	62.35	79.22	35.1	40.75	140.92

The reactions were carried out under unimolecular conditions, keeping the concentration of substrate always high. The reaction was found to be first order with respect to PRL in each case of study, as evidenced by the linear plot of log K_1 vs log [PRL] with a slope of unity. Keeping [PRL] in excess, plot of log [oxidant] vs time was linear with a slope of unity (columns 1, 2, 6 and 7 of Table 1). As concentration of PDC increases, a progressively smaller portion of the total amount is in the form of monomeric chromium(VI) ion and hence the rate constant decreases with increase in [Cr(VI)]. Increase of percentage of acetic acid increases the rate perhaps of the formation of acetochromate ion $AcOCrO_3$[22,23](Column 3 of Table 1). Using PDC, added salt ($NaClO_4$) has no promising effect, but in CBT reaction there is a predominant primary salt effect (Columns 4 and 9 of Table 1). Appreciable decrease in the rate along with the increasing concentration of Mn^{2+} during PDC oxidation (Column 5 of Table 1) suggests an involvement of a two-electron change in its rate determining step[24].

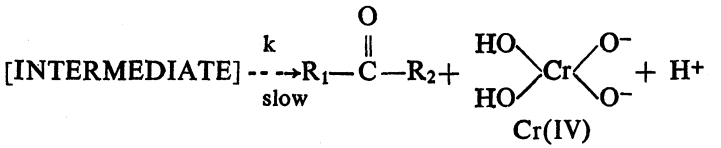
In aqueous acetic acid medium PDC dissociates to give pyridinium ions and chromate ions.

$$(Py^+H)_2Cr_2O_7 + H_2O \rightleftharpoons 2Py^+H + 2HCrO_4^-$$

This chromate ion reacts with alcohols to give the respective ketones. The probable mechanism is



$HCrO_4^-$ Intermediate)



Cr(IV)

When

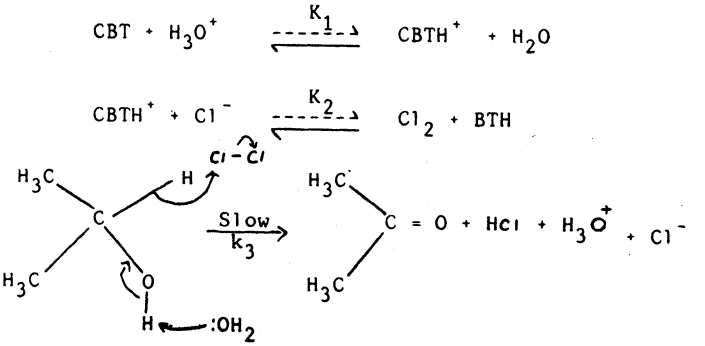
(i) $R_1 = R_2 = CH_3$, 2-Propanol

(ii) $R_1 = CH_3$ and $R_2 = C_6H_5$ PMC

(iii) $R_1 = R_2 = C_6H_5$ = DPC

$$\text{Hence rate} = \frac{-d\,[PDC]}{dt} = kK[\text{alcohol}]\,[PDC]$$

In CBT oxidation, an increase of $[H^+]$ increases the rate of accordance with the expectation[14] based on the involvement of protonated CBT in the mechanism. Increase in rate constant with decrease in dielectric constant is possible only if there is an ion-molecule involvement in the rate determining step. Furthermore, positive salt effect, in presence of added Cl^- showed the interaction of diole-dipole. With $CBTH^+$ as the potent oxidant, the mechanism might assume one or more pre-equilibrium steps for the formation of active oxidant species followed by slow rate determining interaction with an alcohol to give products. It is to be noted that the chloride ion is used only to make reaction rate as measurable.



$$\text{Hence rate} = \frac{-d\,[CBT]}{dt} = \frac{k_3K_1K_2[Cl^-][CBT][H^+][S]}{1 + K_2[Cl^-] + K_1[H^+] + K_1K_2[H^+][Cl^-]}$$

$$\frac{-d[CBT]}{dt} \times \frac{1}{[CBT]} = \frac{k_3K_1K_2[Cl^-][H^+][S]}{1 + K_2[Cl^-] + K_1[H^+] + K_1K_2[H^+][Cl^-]}$$

$$k_{obs} = \frac{k_3K_1K_2[Cl^-][H^+][S]}{1 + K_2[Cl^-] + K_1[H^+] + K_1K_2[H^+][Cl^-]}$$

If K_1, K_2 are very small,

$$k_{obs} = \frac{k_3K_1K_2[Cl^-][H^+][S]}{1+K_2[Cl^-]+K_1[H^+]}$$

$$\frac{1}{k_{obs}} = \frac{2 + K_2[Cl^-] + K_1[H^+]}{k_3K_1K_2[Cl^-][H^+][S]}$$

$$\frac{1}{k_{obs}} = \frac{1}{k_3K_1K_2[Cl^-][H^+][S]} + \frac{1}{k_3K_1[H^+][S]} + \frac{1}{k_3K_2[Cl^-][S]}$$

Under constant [S] and $[Cl^-]$

$$\frac{1}{k_{obs}} = \frac{1}{k_3[H^+]K_1}\left[\frac{1}{K_2[Cl^-][S]} + \frac{1}{[S]}\right] + \frac{1}{k_3K_2[Cl^-][S]}$$

At constant [S] and $[H^+]$

$$\frac{1}{k_{obs}} = \frac{1}{k_3K_2[Cl^-]}\left[\frac{1}{k_1[H^+][S]} + \frac{1}{[S]}\right] + \frac{1}{k_3K_1[H^+][S]}$$

The order of reactivity is DPC $\geqslant$ PMC $>$ PRL (Table 2), when these alcohols are oxidised to their respective ketones there is a change in the hybridization from sp^3 to sp^2 causing a release in steric strain[25,26]. In the case of DPC, two phenyl groups are attached to the same carbon atom causing steric hindrance due to the bulkiness of the phenyl groups. As a result DPC is highly strained compared to PMC and PRL. The strain increases in same order. The least reactivity of PRL is due to the minimum hindrance of two methyl groups. The middle order of PMC is obvious due to the presence of only one phenyl group causing lower strain than in DPL.

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