KINETICS AND MECHANISM OF OXIDATION OF BORNEOL (CYCLIC SECONDARY ALCOHOL) BY TRICHLOROISOCYANURIC ACID IN ACIDIC MEDIUM

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ABSTRACT

The kinetics of Oxidation of borneol ($C_{10}H_{18}O$) [endo-1, 7, 7-Trimethyl bicyclo (2, 2, 1) heptan-2-ol] by aqueous perchloric system, yields of ketone in the presence of Trichloroisocyanuric acid at 300C. The stoichiometry is (1:1) and the main oxidation product is Camphor which is studied by TLC using benzene as a solvent and by spraying with 2, 4-dinitrophenyl hydrazine reagent. The observed rate of oxidation shows a first order dependence on both borneol and TCICA (Oxidant).
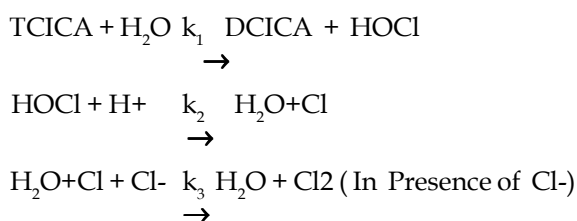
INTRODUCTION

Oxidation of organic compounds is one of the most important reaction in organic synthesis. For this purpose, some new oxidizing reagents have been prepared1-[3]. In the recent years, studies of oxidation of various organic compounds in presence of perchloric acid by halo-compounds[4]. Borneol is a white crystalline bicyclic terpene alcohol and a component of many essential oils [5] and it is natural insect repellent.[6] Borneol is easily oxidized to ketone and occurs in two enatiomeric forms in which the hydroxyl group is placed in an endo-position (Borneol) and an exo-position (Iso-borneol). Borneol is used in traditional Chinese medicine as moxa. Oxidation of cyclic secondary alcohol to carbonyl compound is an organic functional group transformation and numerous reagents and experimental procedures have been developed for oxidation of alcohols to carbonyl compounds[7]. The oxidation of cyclic secondary alcohols have been studied by various oxidants such as N-Bromo-acetamide[8], N-Bromoseccharin[9], N-Chloro R-2, C-6 Diphenyl-t-3 Methyl piperedin-4-on (NCP)[10], Cerium (IV) Catalysed by chromium (III)[11],Cromium (VI) in presence of oxalic acid[12], by aqueous chlorine[13] and oxidation of organic alcohol by pyrazinium dichromate[14]. The Oxidation of Borneol has been studied by chlorine[15] and copper (II)-ß-cyclodextrin in pyridine acetic acid-hydrogen peroxide system[16], but there is no references in the literature on the oxidation of borneol by TCICA. Hence we have undertaken the study of the kinetics of the oxidation Borneol [substrate] with TCICA [oxidant]. Authors studied the kinetics of oxidation of ketones by TCICA in aqueous acetic acid medium in presence of $HClO_4$[17]. The reaction was acid-catalyzed exhibiting first order dependence each in (acid) and (substrate) and zero order dependence in (oxidant). Assuming an acid catalyzed enolisation of ketones in the rate determining step followed by oxidation of enol in a fast step and the

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following rate expression was given

$$\frac{- d\,[\,CTICA\,]}{dt} = K_o\,[TCICA]_o\,[Substrate]\,[H^+]$$

Authors proposed that the nuclear chlorination by Trichloroisocyanuric acid is the first order reaction each in [TCICA] and [substrate] & established the following schemes.

$$TCICA + H_2O \xrightarrow{k_1} DCICA + HOCl$$

$$HOCl + H^+ \xrightarrow{k_2} H_2O + Cl$$

$$H_2O + Cl + Cl^- \xrightarrow{k_3} H_2O + Cl_2\ (\text{In Presence of } Cl^-)$$

By far the most reliable factor for a kinetics study is the effect of concentration. Variation of concentration of a reactant with fixed concentration of other reactants, leads to the determination of order with respect to that reactant, such a study provides information as to what function the rate is of the concentration of that reactant. A review on the functional dependence of the various reactant on the rate, leads to the rate expression [18].

Experimental

The cyclic secondary alcohol (substrate) i.e Borneol (Lancaster) purified by recrystallisation from water and purity was checked by its melting point (208^0C) before use. Trichloroisocyanuric (oxidant) was of Merck made and KI was of AR grade. Other chemicals (reagents) were of spectroscopic grade. TCICA concentration was estimated iodometrically in acid medium in accordance with reaction.

$$C_3O_3N_3(Cl)_3 + 6I^- + H^+ \xrightarrow{} {}_3C_3O_3N_3(H)_3 + {}_3I_2 + {}_3Cl^-$$
$$\qquad (TCICA) \qquad\qquad\qquad\qquad (ICA)$$
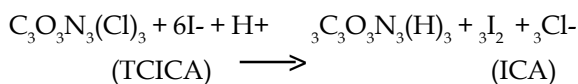
NaClO4 & $HClO_4$ used were of annular grade. The solution of $NaClO_4$ was prepared by direct weighing while that of HClO4 was prepared by dilution and strength was checked by titrating with NaOH using phenolphthalein as indicator. All the experiments were conducted under pseudo first order conditions using more than ten times the concentration of borneol over the concentration of Trichloroisocyanuric Acid [TCICA]. The reaction mixture containing requisite amount of all the reactants i.e. perchloric acid, sodium perchlorate (which is used to maintain the ionic strength of the medium). Borneol and doubly distilled water except oxidant (TCICA) were kept in a corning glass bottle coated on the outside with black japan and wrapped with a black cloth was used as reaction Vessel so as to eliminate the possibility of photochemical effect in the thermostatic water bath at constant temperature 303K. Fresh solution of TCICA was also kept in the same thermo state. After 30 minutes, the required amount of TCICA was added to the reaction mixture. The progress of the reaction is monitored by measuring unconsumed TCICA iodometrically at regular interval of time and poured in the conical flask containing ice-cooled 10% KI solution. After keeping for 10 minutes for liberation of Iodine, the liberated iodine was estimated against a standard solution of sodium thiosulphate with a micro burette using starch solution as indicator. The volume of sodium thio-sulphate corresponding to the iodine liberated by unreacted TCICA was noted. The rate constants (k_{obs}) in replicates were reproducible with in $\pm 5\%$.

Stoichiometric Investigations

Carried out under the conditions [TCICA] = 0.002 mol dm^{-3}, [borneol] =0.001 mol dm^{-3}, [$HClO_4$] = 0.02 mole dm^{-3}, solvent aqueous acetic acid (50%v/v) and temperature 300C were largely not meaningful because of the appreciable decomposition of TCICA, However, the product was identified as camphor by thin layer chromatography using benzene as solvent and by spraying with 2,4 dinitrophenyl-hydrazine reagent.

RESULTS AND DICUSSION

The reaction is first order in [TCICA] as revealed by the constancy of kobs values obtained with different intial [TCICA] and by the linearity of the plot of log [TCICA] vs time. The rate of reaction increases as increase in the [borneol] at fixed [TCICA]. A plot of log kobs vs log [borneol] in linear with unit slop indicating first order dependence in [substrate] Fig. 1. The specific rate increases with an increase in the concentration of by hydrogen ions. Ionic strength is investigated by varing [$NaClO_4$] at constant [$HClO_4$]. Increase in ionic strength of the medium has no significant effect on the specific rate. To determine the temperature coefficient and thermodynamic parameters, the reaction was carried out at different temperature.

A plot of log k_{obs} Vs 1/T (T is the temperature) is
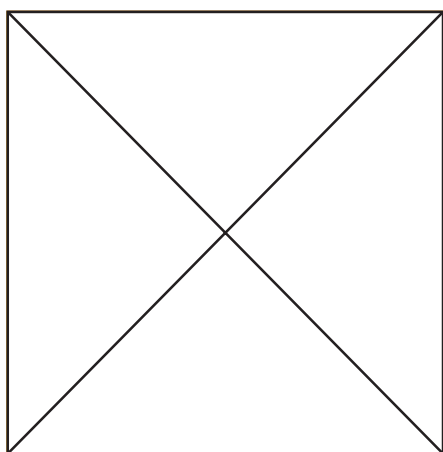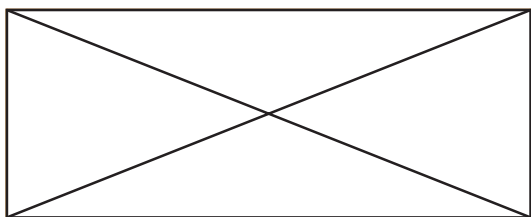
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Fig. 1 Plot of bg k_{obs} Vs. Borneol concentration

linear. Hence the kinetics of the oxidation of borneol by Trichloroisoyanuric acid obey the rate law of first order; in which product camphor (ketone) is formed.

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