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Study of catalytic effect on oxidation of methyl alcohol and ethyl alcohol

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Abstract

Study of catalytic effect on Oxidation of Methyl alcohol and Ethyl alcohol have been studied in acetonitrile medium in the presence of PTSA at 308K temperature. This is due to adsorption of gases or liquids on the surface of the solid and to an activation of the atoms composing the layer next to the surface of the solid. In the search for a catalyst for the oxidation of alcohol, those soluble compounds which form addition compounds with alcohol or with oxygen should be tested as possible homogeneous catalysts. The reaction shows first order dependence with respect to concentration of substrate and [H^+]. The rate of oxidation increases with decrease in dielectric constant of solvent. All experiments were perform at 360nm optical density.

Keywords: oxidation, methyl alcohol, ethyl alcohol

1. Introduction

A catalyst is a substance which can modify the velocity of a reaction without itself undergoing a permanent chemical transformation. If, as frequently happens, the catalyst enters into chemical reaction with one or more of the reactants to form transitory intermediate compounds, it is regenerated in its original chemical form in the final stage of the cycle. By repetition of this cycle a small amount of catalyst is able to effect the conversion of an indefinitely large amount of the reactants [1].

The catalyst probably functions by selectively straining and loosening those bonds of the molecule which will permit the reaction to take place. Catalysts are able to perform this function under conditions of abnormally low thermal activation (lower temperatures); hence, the heat of activation is much smaller. For example, a mixture of H_2 and O_2 is stable at rather high temperatures, but is readily ignited by a platinum sponge at ordinary temperatures. Since catalysts are selective in their action, the reaction can be controlled by them to give the desired product also. There is evidence in many cases that the catalyst first reacts with one of the reacting compounds to form an intermediate compound, which subsequently reacts with the other reacting compound with the regeneration of the catalyst.

$$A + O_2 \rightarrow AO_2 \qquad AO_2 + 2B \rightarrow 2BO + A$$

Catalysts are of two classes, homogeneous and heterogeneous, depending upon whether the catalyst is in the same phase with the reactants or not. Thus, oxides of nitrogen are homogeneous catalysts for the vapor phase oxidation of alcohol, while copper is a heterogeneous catalyst for the same reaction [1].

The efficiency of promoting a reaction as evidenced by the reaction velocity should be proportional to the concentration of a homogeneous catalyst. On the other hand, the efficiency of the heterogeneous catalyst depends more upon the physical state, i.e., fineness of division, character, and extent of surface, than upon the mass of the catalyst.

Alcohols are organic compounds that have one or more hydroxy (-OH) groups bonded to the carbon atoms in aliphatic compounds. They occur widely in nature and have many industrial and pharmaceutical applications. For example, methyl alcohol and ethyl alcohol are two industrially important alcohols.

$CH_3 – OH$	CH_3CH_2-OH
(Methyl alcohol)	(Ethyl alcohol)

Methyl alcohol or methyl alcohol share some similar characteristics with ethyl alcohol or ethyl alcohol. They are colorless liquids, with very good solubility in water. The difference is that methyl alcohol is highly poisonous. Drinking only small amount of methyl alcohol can lead to blindness, or death (10–100 ml). Both methyl alcohol and ethyl alcohol have a pleasant odor.

Ethyl alcohol can be easily confused with methyl alcohol. You can distinguish those two by using the so called *Iodoform* test. In an alkali environment and with iodine the ethyl alcohol will change to acetaldehyde. And acetaldehyde with iodine will provide yellow crystalline iodoform. The methyl alcohol does not react like this.

The oxidation of primary alcohols to carboxylic acids is an important oxidation reaction in organic chemistry. The most common oxidants are PCC, PDC and other Cr (VI) complexes. PCC is known as correy's reagent is very useful oxidizing agent for oxidation of alcohol. It is used as an oxidant for oxidation of alcohols, amino acids, aldehydes, L-cysteine and aniline etc. Oxidation of alcohol by PCC, Dl-alanine by QDC, DL-alanine and Glycine by PDC, L-isoleucine and L-valine by PCC, glycine and alanine by PDC was studied. In this paper we describe kinetics of oxidation of methyl alcohol and ethyl alcohol By PCC in acetonitrile medium. PCC is orange yellow salt which converts in green colored sustains after reduction. As the number of carbon increases rate of oxidation increases [2-20].

2. Material and Method

All chemicals were used of A.R. grade. Purity of alcohol was checked by b.p. PCC is prepared by improved method of Correy and Suggs described. Its purity was checked by m.p. Standard PCC solution was prepared in acetonitrile. All calibrated borosil glassware were used for experiments. Electronic thermostate was used for maintain particular temperature.

Kinetic Measurements: The solution of oxidant, alcohol in non-aqueous solvent in acidic medium follow Beer Lambert's law i.e. absorbance v/s Oxidant is a straight line. The reaction condition are arranged as pseudo first order. The reaction was carried in thermostate in glass stopper at constant temperature. Reaction was initiated by adding rapidly pre-determined volume of PCC solution in above reaction mixture. The optical density of the reaction mixture was measured at 360 nm by using Systronics VISISCAN 167 spectrophotometer.

Product analysis and stoichiometry: Product analysis was carried out under kinetic conditions. The whole reaction mixture (after completion of reaction) was treated with 2, 4-dinitrophenyl hydrazine. A yellow-orange precipitate obtained which was filtered, washed, dried and weighed. Conformation of carbonyl (aldehyde/ketone) compound was done by melting point, IR and nitrogen percentage analysis of precipitate obtained. Cr(III) was confirmed by visible spectra of the reaction solution after completion of reaction. The stoichiometric equation is:

$$3RR'CH(OH) + 2Cr(VI) + H_3O^+ \longrightarrow RR'C = O + 2Cr(III) + H_2O + 7H^+$$

There was no change in rate or absorbance on addition of stabilizer free acrylonitrile in nitrogen atmosphere. This confirms absence of free radical.

Effect of oxidant concentration: The reactions are of first order with respect to PCC i.e. log absorbance versus time is straight line for more than 80% reaction. Further the value of k_{obs} is independent of the initial concentrations of PCC. (Table - 1)

Effect of substrate concentration: The rate of oxidation increased on increasing the concentration of alcohols. Plot of log k_{obs} versus log [substrate] is a straight line (Table - 1). Plot of $1/k_{obs}$ versus 1/[Substrate] gave linear line passing with very small intercepts nearly zero suggests that the rate does not obey Michalis Mentane type kinetics.

Effect of solvent composition: At constant $[H^+]$ the rate of oxidation increases with increase in percentage of solvent composition (Table 3). In other words a decrease in rate with increase in dielectric constant of solvent is observed. This is due to polar character of the transition state as compared to the reactants. The logarithm of the rate constant of a reaction between ions should vary linearly with the reciprocal of the dielectric constant if reaction involves ion-dipole type of interaction. As we increases the ratio of benzene, dielectric constant decrease so that rate of reaction increases.

Effect of temperature: The rates of oxidation of alcohols were observed at various temperature and the reactions obey Arrhenius equation. Energy of activation was calculated by slopes of straight line obtained plotting log k versus 1/T. Suggests the activation parameters for Ethyl alcohol and Methyl alcohol are calculated.

The Mechanism of Chromate Oxidations

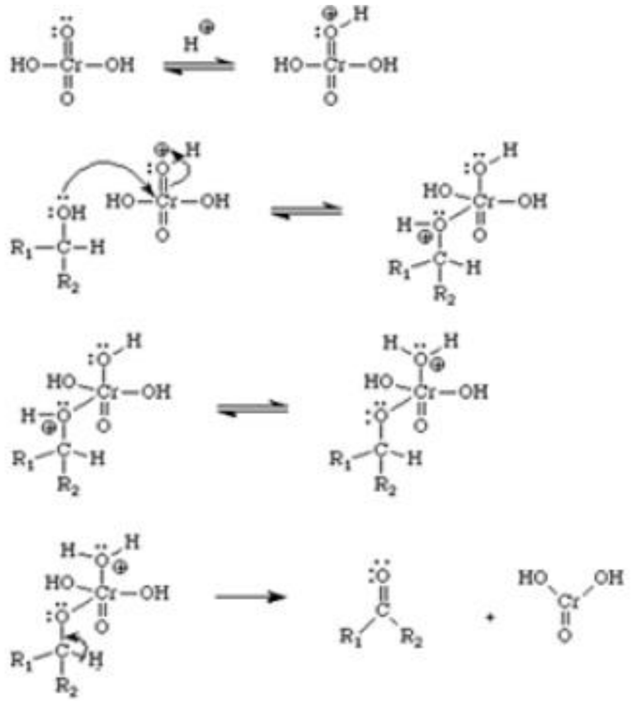

Table 1: Effect of [substrate], $[H^+]$ and Solvent $[PCC]=2\times10^{3}$MT=308K

Subtract x 10^2 mol dm^{-3}	[PTSA] 10^2 mol dm^{-1}	Solvent Acetonitrile + Benzene	k_{obs} x 10^4, sec^{-1}	
			Methyl	Ethyl
2.0	3.0	0	2.51	4.99
3.0	3.0	0	3.41	6.62
4.0	3.0	0	3.97	7.30
5.0	3.0	0	4.57	7.97
6.0	3.0	0	5.05	8.16
7.0	3.0	0	5.37	8.73
8.0	3.0	0	5.44	9.37
9.0	3.0	0	5.65	9.68
2.0	2.0	0	1.16	3.87
2.0	3.0	0	2.51	5.60
2.0	4.0	0	3.92	6.69
2.0	5.0	0	5.65	7.66
2.0	6.0	0	6.20	8.42
2.0	3.0	0	2.51	3.88
2.0	3.0	10	3.6	5.48
2.0	3.0	20	4.07	6.31
2.0	3.0	30	4.70	7.32
2.0	3.0	40	5.67	8.31

Table 2: Variation of rate with temperature [Alcohol] = 2×10^{-2} M,[PTSA] = 3×10^{-2} M, [PCC] = 2×10^{-3} M

Temperature K	$k_{obs} \times 10^4$, sec^{-1}	
	Methyl	Ethyl
298	33.6	50.0
303	51.1	89.7
308	65.5	101.0
313	103.2	135.9
318	122.5	173.0

Table 3: Thermodynamic parameters for various substrate

Substrate	Thermodynamic parameters				
	E_a KJ mol^{-1}	log A	ΔS KJ mol^{-1}	ΔH KJ mol^{-1}	ΔG KJ mol^{-1}
Methyl	51.89	6.89	-98.63	37.4	67.84
Ethyl	45.76	7.92	-97.86	43.2	73.19

4. Discussion

Observations of induced oxidations date from the researches of Schonbein [1], who found that during the autoxidation of many substances, e.g., turpentine and benzaldehyde, for every molecule of oxygen appearing in the reaction product of the primary substance undergoing oxidation an equivalent amount of oxygen was simultaneously transformed to a more active state. This active oxygen could then react secondarily with more oxygen, forming ozone, with water, forming hydrogen peroxide, or with certain other substances-e.g., indigo blue, thus effecting oxidations which could not be effected by ordinary oxygen.

Kinetics of oxidation of Methyl alcohol and Ethyl alcohol by PCC was investigated at particular concentrations of the reactants. At low concentrations of PCC and when substrates are in large excess, the reaction is found to be first order in respect of PCC. Plot of log k_{obs} vs log [Substrate] gave a straight-line with slope ≈1 showed first order dependence over substrate. The thermodynamic parameters are mentioned in Table 3. The entropy of activation is negative as expected for a bimolecular reaction. The rate of oxidation increases with increase in PTSA concentration, increment in temperature and by decreasing the dielectric constant of solvent. Rate of Oxidation of Methyl alcohol is lower than Ethyl alcohol in every condition. This is in accordance with mol and no of carbon atom.

Energy of activation suggests C-H bond breaking in rate determining step and negative entropy of activation indicates formation of cyclic from non-cyclic or more polar than reactants structure formation. A study increase in the oxidation rate with an increase in the acidity of the medium suggests the formation of protonated PCC in the rate-determining step. The plot of log k against log $[H^+]$ is linear with a slope of nearly one suggesting that one protons may involve in the rate determining step.

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