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Kinetics and mechanism of the selective oxidation of primary aliphatic alcohols under phase transfer catalysis

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Kinetics of the oxidation of primary aliphatic alcohols has been carried out using phase transferred monochromate in benzene. Tetrabutylammonium bromide (TBAB) and tetrabutylphosphonium bromide (TBPB) are used as phase transfer catalysts (PT catalyst). The reaction shows first order dependence on both [alcohol] and [monochromate ion]. The oxidation leads to the formation of corresponding aldehyde and no traces of carboxylic acid has been detected. The reaction mixture failed to induce the polymerization of added acrylonitrile which rules out the presence radical intermediates in the reaction. Various thermodynamic parameters have been evaluated and a suitable mechanism has been proposed.

1. Introduction

Chromate and permanganate ions in various forms are used as powerful oxidising agent in organic and inorganic oxidations in polar media.[1-2] Permanganate ions have been used for the oxidation of various organic substrates in non polar solvents under phase transfer catalysis.[3-5] But use of permanganate ion as an oxidising agent does not provide selectivity on product formation. Chromate ion has been found to be used for the selective oxidation of various organic compounds in non-polar solvents under phase transfer catalysis (PTC).[6-10] As a continuation of our earlier work,[11] the present report deals with the selective oxidation of primary aliphatic alcohols (1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol,1-nonanol and 1-decanol) by taking 1-octanol as the typical substrate. The PT catalysts used in the present investigation are tetrabutylammonium bromide (TBAB) and tetrabutylphosphonium bromide (TBPB). The extraction of monochromate into benzene was nearly total (> 95%) when the ratio $Bu_4N^+:Cr_2O_7^{2-}$ was 2:1 in the presence of 0-3 M sulphuric acid. Starks and Liotta[8] had explained the chromate extraction, especially $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$

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into organic medium by using PT catalysts. It is already established that both $HCrO_4^-$ and $HCr_2O_7^-$ can be phase transferred provided the aqueous phase is acidic. But transfer of chromate ions into organic phase cannot be carried out in the absence acid. According to the present study the dichromate anion $Cr_2O_7^{2-}$ is difficult to be transferred into the organic medium due to the difficulty in transferring a bivalent ion.

2. Results and discussion

The sequential scanning of absorption spectra of the reaction system was obtained (Fig. 1) and showed isosbestic points at 333 nm and 394 nm. This clearly shows the formation of a single product and rules out any complex events in the process. The stoichiometry of the oxidation was established by equilibrating known excess concentration of the phase transferred oxidant with known amount of 1-octanol. It was found that one mole of monochromate is equivalent to three moles of 1-octanol.

$$3RCH_2OH + Cr\ (VI) \rightarrow 3RCHO + Cr\ (IV) + 6H^+$$

The product of oxidation, 1-octanal was identified by using various qualitative analytical techniques. The yield of the product was above 90% and no traces of acid has been detected.

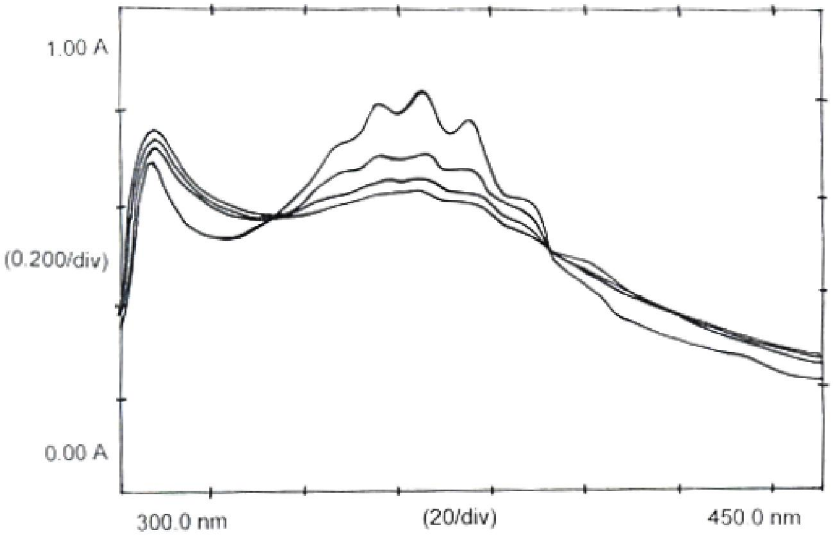


Fig. 1. Absorption spectrum of the successive scans for the oxidation of 1-octanol by $Q^+HCrO_4^-$(Q=TBP) in benzene at 308 K (isosbestic points at 333 nm and 394 nm)

The oxidation of primary aliphatic alcohols by phase transferred monochromate is carried out in an atmosphere of nitrogen and failed to induce the polymerization of added acrylonitrile. This rules out the involvement of any radical intermediate in the reaction.

The rate data of the oxidation of 1-octanol in benzene with different concentrations of the oxidant keeping the [substrate] constant were presented in Table 1. Under the condition when $[RCH_2OH] >> [oxidant]$, the plots of log [oxidant] versus time were found to be linear indicating first order dependence on the [oxidant]. This was further confirmed from the constancy in the values of the specific rates (k_{obs}) for the different concentrations of the oxidant for a given [substrate]. This result is given in the set of k_{obs} values in the first and second rows in Table 1 for two different PT catalysts. The observed rate constants with different [substrate] and the same [oxidant] with both the PT catalysts (set of k_{obs} values given in third and fourth rows of Table 1) increase linearly with increase in [substrate]. Plots of log k_{obs} versus log [substrate] were linear (r = 0.990 and 0.999 for TBPB and TBAB respectively) with a slope of unity and this shows that the reaction is first order in [substrate].

Table 1. Effect of [oxidant] and [substrate] on the rate of oxidation of 1-octanol

Temperature: 308 K Medium: Benzene

[1-octanol]x10^1 (mol dm^{-3})	[$Q^+HCrO_4^-$]x10^3 (mol dm^{-3}) TBPB	TBAB	k_{obs} x10^5 (s^{-1})	$k_2 = \frac{k_{obs}}{[1-octanol]}$ x10^4 (dm^3 $mol^{-1}s^{-1}$)
2.0	4.0	--	4.12	2.06
2.0	5.0	--	4.28	2.14
2.0	6.0	--	4.08	2.04
2.0	8.0	--	4.24	2.12
2.0	--	4.0	3.06	1.53
2.0	--	5.0	3.16	1.58
2.0	--	6.0	3.08	1.54
2.0	--	8.0	3.07	1.53
1.2	5.0	--	2.31	1.93
1.6	5.0	--	3.05	1.91
2.0	5.0	--	4.28	2.14
3.0	5.0	--	5.73	1.91
1.2	--	5.0	1.85	1.54
1.6	--	5.0	2.56	1.60
2.0	--	5.0	3.16	1.58
3.0	--	5.0	4.66	1.56

The effect of temperature on the rate of oxidation of all alcohols was carried out in the temperature range 303 K to 318 K and is presented in Table 2. The values of various activation parameters are also presented in Table 2.

Table 2. Activation parameters for the oxidation of primary alcohols

Medium: Benzene [$Q^+HCrO_4^-$] x 10^3 = 5.0 mol dm^{-3} [RCH_2OH] x 10^1 = 2.0 mol dm^{-3}

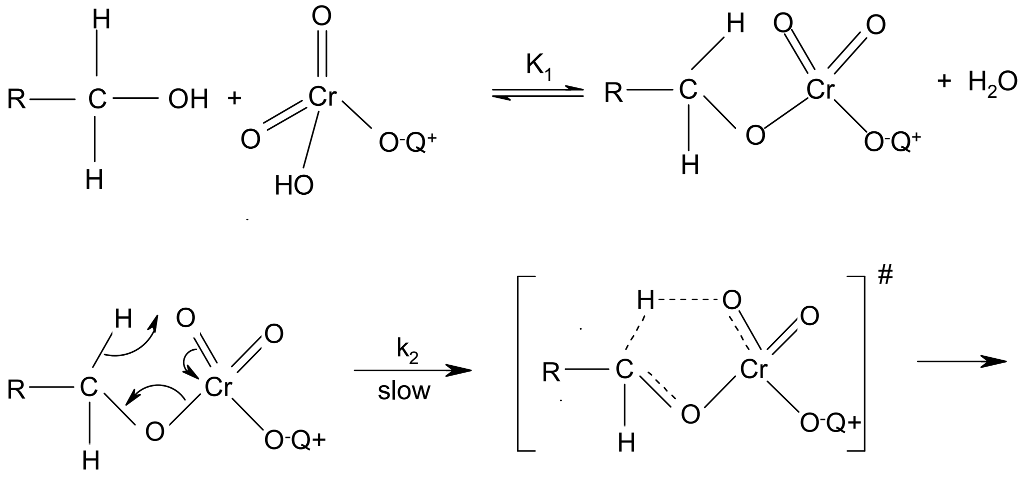
Substrate	PT catalyst	k_2 x 10^5 (dm^3 mol^{-1} s^{-1}) at temp K 303	308	313	318	Ea (kJmol^{-1})	$\Delta H^\#$ (kJ mol^{-1})	$-\Delta S^\#$ ($JK^{-1}mol^{-1}$)	$\Delta G^\#$ (kJ mol^{-1})
1-butanol	TBPB	9.63	11.5	14.3	17.3	31.4	28.8	226	97.5
	TBAB	6.94	10.1	11.8	13.7	35.4	32.8	216	98.4
1-pentanol	TBPB	13.4	16.9	21.3	23.7	31.3	28.7	224	96.7
	TBAB	8.48	11.1	13.4	16.7	35.6	33.0	214	97.9
1-hexanol	TBPB	14.5	18.1	22.3	25.5	30.7	28.1	225	96.5
	TBAB	9.89	12.7	16.0	19.2	35.5	32.9	213	97.5
1-heptanol	TBPB	15.6	19.7	23.2	27.5	30.0	27.4	227	96.4
	TBAB	10.9	13.5	16.0	21.4	34.9	32.4	214	97.2
1-octanol	TBPB	15.7	21.4	25.0	27.8	30.1	27.5	227	96.3
	TBAB	12.8	15.8	19.3	24.7	34.9	32.4	213	96.9
1-nonanol	TBPB	16.6	21.3	25.6	29.1	30.0	27.4	227	96.2
	TBAB	13.9	15.8	21.2	25.8	34.5	31.9	213	96.7
1-decanol	TBPB	17.3	21.4	26.2	30.2	30.1	27.5	226	96.0
	TBAB	14.2	19.1	23.3	27.3	34.7	32.1	212	96.6

The anionic species ($HCrO_4^-$) formed in the given acidic aqueous medium gets phase transferred to the organic medium as an ion-pair ($Q^+HCrO_4^-$) in the presence of PT catalyst. The reaction may proceed in the organic medium through the interaction of phase transferred oxidant with the substrate alcohol to form a complex which subsequently disproportionate to the product. The formation of chromate ester as an intermediate in a pre-equilibrium step has been reported elsewhere.[6-7] The interaction of ^{2}P- electrons on the HOMO of oxygen in alcohol with LUMO of the chromium enables the formation of chromate ester.[13] The rate determining step is the decomposition of the chromate ester via cyclic Huckel type transition state and it involves the ruptures of ά C-H bond and O-Cr bond forming the product.[14-15]

It has been reported that the chromate ester has greater stability in organic solvents than in water.[16-17] The large negative $\Delta S^\#$ values implies the formation of a chromate ester with a high degree of orderedness supporting cyclic intermediate formation. Bordwell[18] had ruled out the occurrence of concerted one step bimolecular process by hydrogen transfer and in the present studies also the hydrogen transfer does not occur by an acyclic bimolecular process. It is already reported that intrinsically concerted sigmatropic reactions, characterized by transfer of hydrogen in cyclic transition state are the only truly symmetrical processes involving a linear hydrogen transfer.[13] Littler[19] had shown that a cyclic hydride transfer is occurring in the oxidation of alcohols by Cr (VI) with six electrons and being a Huckel type system it is an allowed process. Thus a planar, cyclic and symmetrical transition state can be envisaged for the decomposition of the ester intermediate. The overall mechanism proposed is involving the formation of a chromate ester in a fast pre-equilibrium step and then decomposition of the ester intermediate in a subsequent slow step via a cyclic concerted symmetrical transition state giving the product. The mechanism proposed is presented as

$$[Q^+HCrO_4^-]_{H_2O} \rightleftharpoons [Q^+HCrO_4^-]_{org}$$

The phase transferred $Q^+HCrO_4^-$ reacts with alcohol in the organic medium as follows.



RCHO + Cr(IV) + H_2O + H^+

$$3Cr(IV) \longrightarrow Cr(VI) + 2Cr(III)$$

Cr (IV) formed in the reaction is unstable in the organic medium and undergoes fast disproportionation to Cr (III).

A suitable rate expression for the oxidation of primary aliphatic alcohols using phase transferred monochromate in consistent with the above mechanism can be given as:

$$\frac{-d[HCrO_4^-]}{dt} = k_2[\text{complex}] = K_1k_2\,[RCH_2OH]\,[HCrO_4^-]$$

3. Conclusions

The selective oxidation of primary aliphatic alcohols involves the formation of chromate ester which on decomposition giving the product. It is not possible to carry out the reaction in organic media without using PT catalysts. So this method involving PT catalysts can be used for the selective oxidation of primary alcohols in non-polar solvents and hence kinetics and mechanism can be easily studied.

4. Experimental

4.1 Materials and methods

Analar grade potassium dichromate was used. Alcohols and benzene were purified by standard methods.[12] Doubly distilled water was used throughout this study. The extraction of monochromate into benzene was carried out in the presence of 2.0 mol dm^{-3} sulphuric acid using TBPB and TBAB as PT catalysts.

4.2 General procedure

Monochromate ion has been phase transferred by equilibrating aqueous potassium dichromate (0.05 mol dm^{-3}) with pure benzene containing TBAB or TBPB (0.1 mol dm^{-3}) in the presence of 2.0 mol dm^{-3} H_2SO_4. The organic layer containing oxidant was separated and dried over anhydrous sodium sulphate. The oxidant concentration was estimated by spectrophotometric method. This oxidant solution is found to be stable for more than ten hours enabling convenient kinetic study. A known volume of $Q^+HCrO_4^-$ was mixed with known volume of benzene and the mixture was thermostated for 20 minutes at the desired temperatures. To this reaction mixture required volume of previously thermostated alcohol in benzene was added using a calibrated pipette.

4.3 Kinetic measurement

The kinetic measurements were carried out under condition where $[RCH_2OH] >> [Q^+HCrO_4^-]$ where Q^+ is quaternary onium cation. The progress of the reaction was followed spectrophotometrically using a Schimadzu 1601 UV-Visible spectrophotometer by measuring the absorbance of $HCrO_4^-$ ions at 365 nm. The experiments were repeated and the pseudo-first order rate constants k_{obs} were computed from the linear least squares plots of log $[HCrO_4^-]$ versus time.

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