Notes

Kinetics and mechanism of oxidation of aliphatic acetals with peroxomonosulphate

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The oxidation of fifteen aliphatic acetals of normal aliphatic aldehydes and substituted aliphatic aldehydes with aliphatic and substituted aliphatic as well as with aromatic alcohols by peroxomonosulphate in aqueous acetic acid medium is first order each in [oxidant] and [acetal] and yields the corresponding esters as the main product. The oxidation reaction is independent of change in dielectric constant of the medium. The activation enthalpies and entropies of the reactions are linearly related. A mechanism involving hydride ion shift is proposed.

A detailed literature search revealed that eventhough considerable attention has been focussed on the oxidation of acetals with peracetic acid[1], oxidation of cyclic acetals with excess of chromic acid in acetic acid[2], kinetics of oxidation of aliphatic[3] as well as aromatic acetals[4] with chromic acid in aqueous acetic acid medium, kinetics of oxidation of aliphatic acetals with lead (IV) acetate in acetic acid, in aqueous acetic acid and in acetic acid-benzene medium[5], kinetics of oxidation of aliphatic acetals with N-chlorosaccharin in aqueous acetic acid medium[6] and kinetics of oxidation of aliphatic acetals with N-chlorobenzamide in aqueous acetic acid medium[7] there seems to be no report on the kinetics of oxidation of aliphatic acetals by peroxomonosulphate in aqueous acetic acid medium. Hence the kinetics of oxidation of aliphatic acetals of normal aliphatic aldehydes and substituted aliphatic aldehydes with aliphatic, halogen substituted aliphatic and aromatic alcohols by peroxomonosulphate have been studied in aqueous acetic acid medium with a view to probe the mechanism of oxidation.

Experimental

Peroxomonosulphate (PMS) supplied by du Pont de Nemours was used as such. Maruthamuthu and Neta reported that the compound was 96% pure[8] and further attempt to purify the compound lead to fail-

ure. Acetaldehyde diethyl acetal (AEA), monochloroacetaldehyde diethyl acetal (mCAEA) and dichloroacetaldehyde diethyl acetal (dCAEA) were imported samples. Acetaldehyde di-n-propyl acetal (AnPA), acetaldehyde di- n-butyl acetal (AnBA), propionaldehyde diethyl acetal (PDEA), n- butyraldehyde diethyl acetal (nBEA), isobutyraldehyde diethyl acetal (iBEA), iso-butyraldehyde di-n-butyl acetal (iBnBA), acetaldehyde dibenzyl acetal (ABA), propionaldehyde dibenzyl acetal (PBA), monochloroacetaldehyde dibenzyl acetal (mCABA), acetaldehyde diethylenechlorohydrin acetal (AEChA), n-butyraldehyde diethylenechlorohydrin acetal (nBEChA) and monochloroacetaldehyde diethylenechlorohydrin acetal (mCAEChA) were prepared by the standard procedure and their purities were checked by the usual methods.

The reactions were studied under pseudo-first order conditions ([acetal]>>[PMS] in acetic acid 40, 50, 60, 65, 70, 75, 80 and 90%) v/v) and the kinetic of the reaction were followed by monitoring the disappearance of PMS by iodometry at different intervals of time. The rate constants were computed from the linear ($r>0.98$) plots of log [oxidant] against time. The results were reproducible within ± 3%. Under the conditions of the experiment, the solvents were not oxidised. The second order rate constant k_2 was obtained from the relation $k_2 = k_1/[acetal]$, where k_1 is the pseudo-first order rate constant. the method of least squares was employed to estimate the uncertainties in the kinetic and thermodynamic parameters.

Product analysis

The product analysis was carried out as under the kinetic conditions. ABA (24.2g, 0.1M) and PMS (6.14g, 0.01M) were made upto 100mL with 50, 75 and 90% (v/v) acetic acid keeping ionic strength (0.2M) constant. mCABA (27.6g, 0.1M) and PMS (6.14g, 0.01M) were made upto 100mL with 50, 75 and 90% (v/v) aceticacid keeping ionic strength (0.2M) constant. The reaction mixtures were allowed to stand 12h to ensure completion of the reaction. The following procedure was adopted for each sample.

The solutions were diluted and extracted with ether. The ether extracts were dried over anhydrous

Table 1 - Effect of substituents on rate constants and activation parameters.

[Acetal] = 2.5 X 10^{-2} mol dm^{-3}; [PMS] = 2.5 X 10^{-3} mol dm^{-3}; I = 0.2 mol dm^{-3}; (Solvent = HOAc (80% v/v)

Acetals	$10^2 k_2$ (dm^3 mol^{-1} s^{-1})				$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (J deg^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
	308	318	328	338			
AEA	3.30	4.86	7.75	13.70	39.0	148.6	84.8
AnPA	1.10	1.62	2.30	3.17	28.2	192.8	87.6
AnBA	0.73	1.16	1.60.	2.47	32.2	183.6	88.7
nBEA	1.22	1.90	2.86	4.21	33.6	174.6	87.3
ABA	2.98	4.73	7.32	10.84	35.0	162.3	85.0
PEA	2.12	3.25	4.70	8.12	35.7	163.0	86.0
PBA	1.32	1.90	3.50	5.00	37.6	160.7	87.2
iBEA	0.11	0.21	0.37	0.68	50.0	141.5	93.5
iBnBA	0.71	1.05	1.67	2.53	35.0	176.0	88.8
mCAEA	0.14	0.36	0.85	1.90	72.0	67.6	92.8
dCAEA	0.14	0.31	0.66	1.32	62.7	98.1	93.0
mCABA	0.05	0.10	0.16	0.27	43.0	169.6	95.0
AEChA	1.30	1.78	2.46	3.31	24.8	202.5	87.2
nBEChA	1.72	2.63	3.90	5.75	32.8	174.3	86.4
mCAEChA	0.07	0.12	0.60	1.05	81.4	43.3	94.6

sodium sulphate and solvents were removed under pressure. The product mixtures were then analysed by GLC combined mass spectra. The mass spectra clearly indicated the presence of benzyl acetate or rather benzyl cation as the main product of oxidation and no peak was observed for the presence of dibenzylsulphate. Further TLC and GLC analysis showed the presence of corresponding esters as the main product of oxidation. The possibility of formation of diaryl sulphates or dialkyl sulphates in all probability can be ruled out since they may likely to be present as ions. The products in each case were characterized by direct comparison with authentic samples as the corresponding esters (70-80% yield).

Results and discussion

The kinetic results can be summarised as follows.

i. The reaction was found to be first order in oxidant. Individual kinetic runs were strictly first order with respect to PMS. Further the first order rate coefficients did not vary with the initial concentration of PMS. The order in acetal is also one.

ii. As is generally observed in PMS oxidation[9,10], changes in water content of the system did not affect the rate of the oxidation, thus showing that the change of dielectric

constant of the system does not affect the rate of oxidation.

iii. Freshly distilled acrylonitrile monomer when added to the deaerated reaction mixture did not polymerise.

iv. The absence of effect of ionic strength on reaction rate suggests[11] that the reaction should involve atleast one neutral species, namely, the acetal molecule, since the mononegative anion HSO$^-_5$ is known to be the active species of the oxidant[12].

v. The addition of sodium acetate and sodium chloride did not appreciably alter the rate.

vi. The rate data have been collected in the temperature range 308K to 338K and the activation parameters calculated from the least squares slopes of logk_2 versus 1/T (Table 1).

The observed kinetic results can be rationalised on the basis of the mechanism outlined in Scheme 1.

Scheme 1 involves the hydride ion shift, which explains the appreciable rate decrease in the case of mCAEA and dCAEA, when compared to unsubstituted acetals (Table 1). The introduction of chlorine atoms both in the aldehyde part as well as in the alcohol part leads to further decrease in rate of oxidation as observed in mCAEChA, lends a favourable
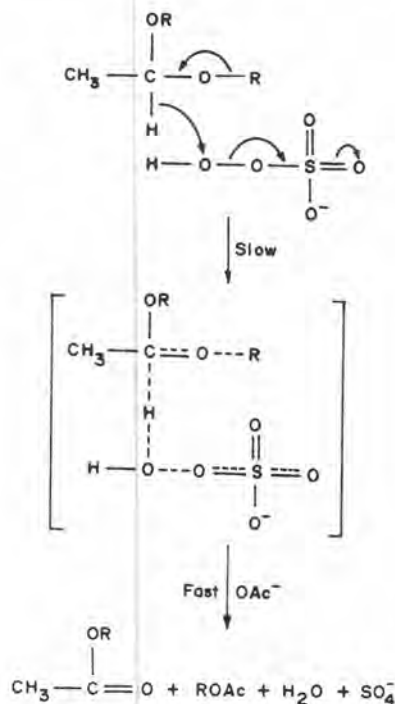
Scheme 1

support to Scheme 1. Which explains the observed solvent influence on the rate of oxidation and the kinetic order observed.

Since changes in the nature of the alcohol part of the molecule profoundly affect the rates as compared to the changges in the aldehydic part, in may be inferred that the effect of change in structure operates on the alkyl carbon, rather than on the aldehyde carbon atom (Table 1).

The linear correlation between the activation enthalpies and entropies ($r > 0.98$, 356K) suggests that all the aliphatic acetals are oxidised by the same mechanism and the changes in the rates are governed by changes in both enthalpies and entropies of activation (Table 1).

Acknowledgement

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