Kinetics of Aldehyde Oxidation on Platinum Anode in Aqueous Perchloric Acid & Sulphuric Acid

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Kinetics of aldehyde oxidation on platinum anode surface has been studied in aqueous $HClO_4$ and sulphuric acid. The correlation between first order rate constants and acidities of the solutions has been worked out. The values of the parameters w_0 and φ (w_0 and φ_0 in this case) have been evaluated on the lines previously suggested. A reaction mechanism involving protonation of the aldehyde, reaction of the protonated form with oxygen and finally reaction with water to yield the products has been suggested.

IN the presence of mineral acids like HCl, H_2SO_4 or $HClO_4$ many chemical reactions exhibit a change in the reaction rate or in the equilibrium as the [acid] is changed. Hammett *et al.*[1,2] suggested that these effects can be explained on the basis of the concept of acidity functions. According to these authors, if the rate constant k varied linearly with the acidity function, H_0, the conversion of the protonated substrate SH^+ to the transition state does not involve interaction with water. If log k varied linearly with log [HX] the same transformation required several molecules of water. The possiblity that the transition state in case of some acid-catalysed reactions may involve participation of several molecules of water was also suggested by Listen[3].

In a different approach Bunnett[4] studied a large number of hydrolytic reactions (over 150) and found that the plots of log $k\Psi+H_0$ versus log a_{H_2O} were linear. Slopes of these plots provided a new parameter W and the different numerical w values were suggestive of different reaction mechanisms.

Bunnett and Olsen[5,6] further observed that the effects of changing the acidity of the medium on the equilibria or the rate constants can also be viewed from the free energy relationship. They suggested another approach where log k $+H_0$ was plotted against H_0+ log $[H^+]$ instead of log a_{H_2O}. The slope in this case was called ϕ, a parameter whose values appear to acquire more important significance than the W value[4].

The equilibrium protonation of a substrate [S] is represented as $S+H^+ \rightleftharpoons SH^+$ and the equilibrium quotient $Q=[SH^+]/[S][H^+]$. Q is the reciprocal of the equilibrium constant for acid dissociation of SH^+, log Q thus becomes the thermodynamic pK_{SH^+} for that substrate in that medium.

It was shown by Bunnett and Olsen[5,6] that linear free energy relationship exists betweeen logarithms of equilibrium quotients and rate constants. The slope ϕ of the linear plots characterizes the response of equilibrium quotient Q to the changing acid concentrations whereas its intercept represents

the thermodynamic pK_a of the base. It thus provides a general method for estimating pK_a of any base which undergoes protonation in moderately concentrated mineral acids.

This work has been planned to study the effect of the extent of protonation on the rate of electrolytic oxidation or reduction of aldehydes on polished platinum anode or cathode in solutions of different acidities. Some important findings of this investigation are reported here.

Materials and Methods

The aldehydes studied were: (i) formaldehyde, (ii) acetaldehyde and (iii) propionaldehyde (all of BDH, AR grade) and were purified if necessary by fractionation. Investigation was carried out in a cell where the anode and the cathode compartments were separate but were joined to one central compartment through sintered glass partition. Polished platinum electrodes (area 1 cm²) were placed in the compartments and once fixed would maintain a constant position. Pure nitrogen bubbling very slowly in each compartment maintained an atmosphere of nitrogen and also stirred the solutions. The platinum foil electrodes were carefully polished with a suspension of alumina in ethanol and then washed thoroughly with distilled water before each experimental run. The reactions were studied at various acid concentrations of (i) $HClO_4$ and (ii) H_2SO_4. A direct current in a range of 50 to 250 ma/cm² was passed through the electrolytic solution.

Reaction mixture (~100 ml) was taken in a cell for every experiment. The system was thermostated throughout the run. The rate of disappearance of aldehyde in each electrode compartment was measured separately. However, the resoponse of the reaction to the changing acid concentration and the temperature, only in the anodic compartment is reported here. At known intervals, an aliquot solution (1 ml) was removed from the electrode compartment and analysed for its aldehyde content. These were estimated colorimetrically with

MBTH (3-methyl-2-benzothiozolinone hydrazone hydrochloride monohydrate) which forms a brilliant blue cationic dye in the presence of ferric chloride and sulphamic acid. This method is very sensitive for determination of water-soluble aliphatic aldehydes[8]. The reaction was carried out at three different temperatures, viz. 30°, 40° and 50° respectively. The rate constants 'k' were calculated considering the reaction to be of first order with respect to [aldehyde].

Results and Discussion

An analysis of the results brings out the following important features.

(i) On passing current through the solution aldehyde disappeared from both the electrode compartments and the rates of disappearance of aldehyde (in both the compartments) was found to follow first order rate law.

(ii) The rate constants were found to depend upon the [acid]. With increase in [acid] the rate was found to increase in the initial stages only up to a certain specific concentration of the acid which depended on the nature of the acid (Fig. 1). The rate constant, thereafter, decreased with further increase in [acid].

(iii) The rate constants increased with increase in temperature but the [acid] at which the rate maximum was observed was found to be the same.

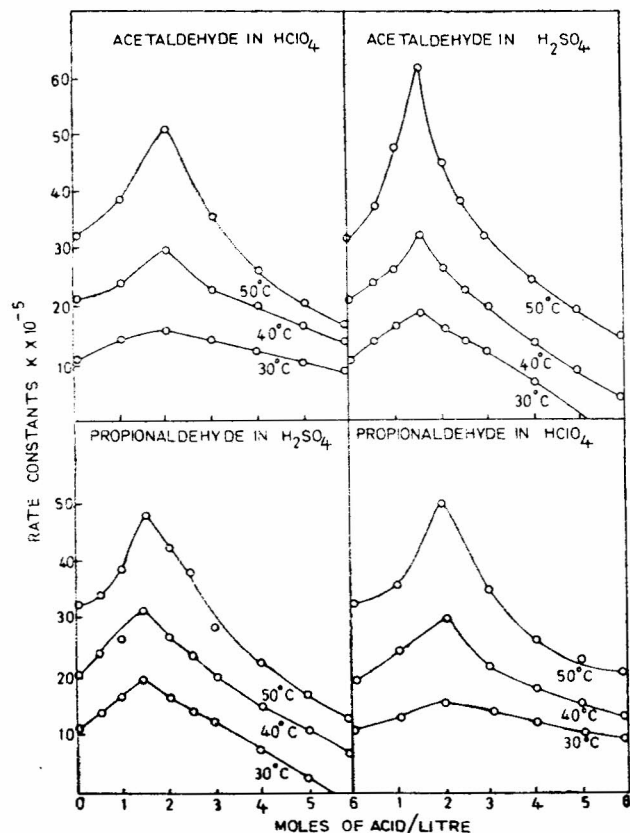(iv) The energy of activation and the entropy changes of the reaction were also calculated and are listed in Table 1.

Fig. 1 — Dependence of rate constant on acid concentrations

TABLE 1 — ACTIVATION PARAMETERS FOR THE ELECTRODE REACTIONS OF ALDEHYDES

Acid	$\Delta H^{\ddagger}$ kcal/mol at		$\Delta S^{\ddagger}$ e.u. at	
	40°	50°	40°	50°
FORMALDEHYDE				
H_2SO_4	13·168	10·376	−38·00	−47·30
$HClO_4$	11·625	11·265	−41·85	−43·177
ACETALDEHYDE				
H_2SO_4	10·530	9·825	−42·579	−44·917
$HClO_4$	9·584	8·713	−45·994	−48·795
PROPIONALDEHYDE				
H_2SO_4	9·763	9·164	−37·758	−39·778
$HClO_4$	9·768	9·292	−39·193	−40·154

For explaining the reaction mechanism Bunnett[9] and others[10] considered the change in the hydration as a very important factor. The support for this change in the hydration postulate was derived from the interrelationship between the entropy values and the w values. However, factors not related to solvation change are known to affect the entropy of activation. The rate maxima for specific concentration of the acid is also observed in several other cases like the carboxylic amide hydrolysis[11]. In such reactions it is recognized that the substrate gets progressively protonated and the protonation is almost complete where the acid concentration shows highest k value. Similar results have also been reported by Rosenthal and Taylor[12].

A good deal about the mechanism of the reaction can be learnt from its kinetics under various experimental conditions. Besides, a lot of additional information can be obtained by determining the rate of reaction for a series of reaction compounds. The results obtained during the anodic oxidation of three aldehydes (i.e. reaction taking place only in the anode compartment) are presented in Table 2.

In the analysis that follows the first order rate constant is represented by symbol k. Its dependence on the [H^+], the acidity and the amount of water, is brought out in two independent ways by plotting (i) $\log k + H_0$ against a_{H_2O} (Fig. 2) and (ii) $\log k + H_0$ against $H_0 + \log$ [H^+] (Fig. 3). The slopes of these plots in the present case are designated as w_0 and ϕ_0 (signifying the oxidative process) respectively which in the case of hydrolytic reactions were designated as w and ϕ by Bunnett and Olsen[5,6].

With increasing [acid] the k values rise smoothly, reach a maximum and then gradually fall off. The above-mentioned plots can thus be shown to consist of two distinct straight lines with a point of inflexion marking the maximum k value (Fig. 1). Each of these plots will, therefore, have two slope values, one pertaining to the relation where k increased with [acid] and the other where k decreased with increasing [acid]. Following earlier convention, these values of slopes are also designated as w_{OA}, w_{OB} and ϕ_{OA}, ϕ_{OB}, values for the oxidative reactions. The results are included in Table 3.

TABLE 2 — DEPENDENCE OF THE REACTION RATES ON ACID CONCENTRATIONS

(Current density, 50 mA/cm^2)

[Acid] M	Formaldehyde in H$_2$SO$_4$ ($k \times 10^{-6}$) at			Acetaldehyde in H$_2$SO$_4$ ($k \times 10^{-5}$) at			Propionaldehyde in H$_2$SO$_4$ ($k \times 10^{-5}$) at		
	30°	40°	50°	30°	40°	50°	30°	40°	50°
0·0	22·5	45·1	88·1	10·8	21·16	32·5	10·6	19·2	32·2
0·5	24·8	53·3	89·3	13·7	24·0	35·2	14·2	24·3	35·2
1·0	31·1	60·0	93·5	16·1	26·3	47·7	16·2	26·3	39·2
1·5	22·0	46·6	75·0	18·5	32·6	61·7	19·5	31·5	47·7
2·0	18·6	36·6	65·1	15·0	26·3	45·0	15·8	26·2	42·0
2·5	17·6	35·0	55·6	13·6	22·7	38·5	13·6	23·5	38·5
3·0	15·0	32·6	52·3	12·1	19·7	32·5	12·3	19·8	28·3
4·0	9·0	26·0	41·0	6·5	14·0	25·0	7·0	14·5	22·0
5·0	4·0	18·0	32·0	1·0	10·5	19·0	2·0	10·5	17·0
6·0	—	12·0	22·0	—	4·0	14·5	—	6·0	12·0
7·0	—	5·0	12·0	—	—	—	—	—	—
	Formaldehyde in HClO$_4$			Acetaldehyde in HClO$_4$			Propionaldehyde in HClO$_4$		
0·0	22·5	45·1	88·1	10·8	21·2	32·5	10·6	19·0	32·0
1·0	20·5	57·1	92·8	14·2	24·2	38·5	12·5	24·0	36·3
2·0	34·8	60·0	113·1	15·6	29·8	51·2	15·0	29·8	50·1
3·0	37·1	70·0	120·5	13·8	22·7	35·2	13·7	21·3	34·7
4·0	40·1	75·0	138·3	12·2	19·5	26·3	11·6	17·5	26·3
5·0	36·1	61·8	109·3	10·1	15·6	20·8	10·0	15·0	22·0
6·0	30·8	60·0	101·1	8·7	13·8	17·0	8·3	13·0	21·2
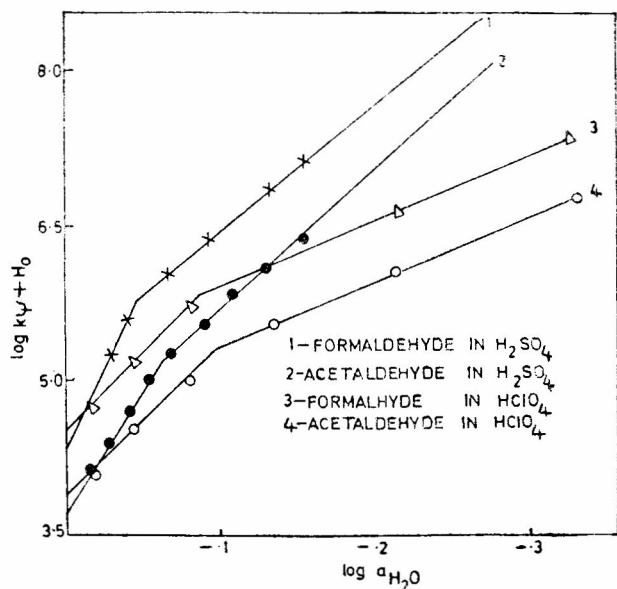
Fig. 2 — Variation of log $k + H_0$ with a_{H_2O}
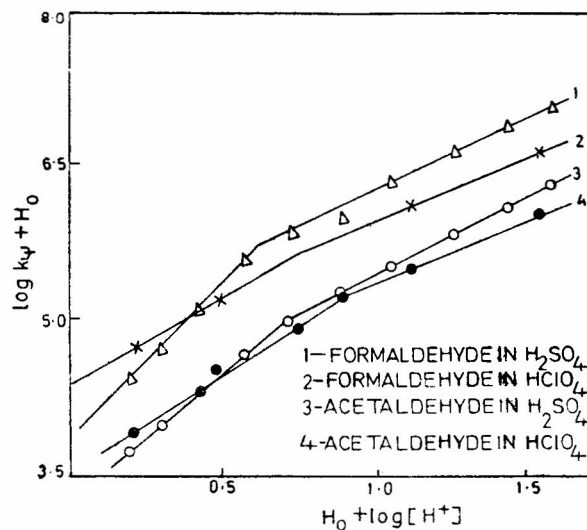
Fig. 3 — Variation of log $k + H_0$ with $H_0 + \log [H^+]$

Bunnett and his coworkers[4,5] on the basis of generally accepted mechanisms for certain calibration reactions considered certain values of w and ϕ as suggestive of the role of water in the reaction sequence. These values are given in Table 4.

Reaction mechanism — Based on our observations the mechanism of the reaction appears to involve the steps shown in Scheme 1.

(i) The rate of the reaction increases initially with [acid]. This suggests that the protonated form of the aldehyde whose concentration increases with increasing concentrations of the acids, is one of the reaction species. Two tautomeric structures (A) or (B) of the protonated aldehyde are possible.

(ii) The protonated form reacts with oxygen, which could be either at the electrode surface or in the bulk of the solution if a suitable carrier for oxygen is present[10].

(iii) Since there is a smooth fall in the rate constant after the specific acid concentration is reached the reaction appears to be influenced by the decreasing concentration of water. Hence it is suggested that for the conversion of the product

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TABLE 3 — VALUES OF w_0 AND ϕ_0 AT 30°

Acid	ϕOA	ϕOB	wOA	wOB
	FORMALDEHYDE			
HClO$_4$	1·725	1·25	17·2	6·6
H$_2$SO$_4$	3·075	1·41	33·0	12·3
	ACETALDEHYDE			
HClO$_4$	1·85	1·26	15·0	6·3
H$_2$SO$_4$	2·40	1·56	25·0	13·8
	PROPIONALDEHYDE			
H$_2$SO$_4$	2·55	1·48	22·7	11·2

TABLE 4 — w AND ϕ VALUES FOR SUBSTRATES PROTONATED ON OXYGEN OR NITROGEN

w values	ϕ values	Role of water in the rate detg step
−2·5 to 0·0	<0·0	Water is not involved
+1·2 to 3·3	+0·22-0·56	Water acts as a nucleophile
>+3·3	>0·58	Water acts as a proton transfer agent

Scheme 1

in stage (ii) to the final product, water must be an essential constituent.

It will be observed that the w_0 and ϕ_0 values obtained by us in the anodic oxidation of aldehydes are numerically very different from values of w and ϕ reported by Bunnett for the hydrolytic reaction. It is likely that for the oxidative process which we have studied these norms of w and ϕ values suggestive of the role of water may be higher. Further experimentation with new systems and similar analysis of the cathodic disappearance of aldehydes are necessary to throw more light on the utility of this approach.

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