ANODIC OXIDATION OF AROMATIC ACETALS

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Aromatic acetals have been electrochemically oxidised in non-aqueous medium, at Platinum anode. The major product is reported to be the corresponding esters, which are characterized spectroscopically. A probable mechanism for oxidation is proposed.

Earlier studies on the oxidation of both aliphatic and aromatic acetals under photochemical, pyrolytic and chemical conditions employing a vide range of oxidising agents [1-4] propose the formation of the corresponding esters, ethers, aldehydes, acids etc Both kinetic and mechanistic approaches are dealt with extensively.

The electrochemical oxidation of acetals of benzaldehyde containing different alcoholic fragments - ethyl, n-butyl and amyl, have been studied here, in non-aqueous mediu , at platinum electrode. The results show that electrochemical oxidation is far superior to the other, thermal, photochemical and the conventional chemical methods. Here esters - alkyl benzoates-are found to be the exclusive products, and in better yields, with traces of benzaldhyde and benzoic acid.

It is observed that the supporting electrolyte employed, has a special role to play, as a reaction initiator besides its prime character of conductor of electric current. This is similar to the behaviour already reported in electrochemical alkoxylation of cyclic ethers [5], acetoxylation of mesitylene and toluene [6], oxidation of alcohols [8-9], oxidation of side chain in aromatic compounds [7] and a number of radical initiated polymerization processes. In these studies ammonium nitrate, potassium iodide iodine, perchlorates of sodium and lithium tetra-alkyl ammonium salts etc. have been employed as the supporting electrolytes. Under specific electrode potentials, potassium iodide and iodine are reported to initiate electrochemical oxidations of alcohols, ethers and other organic compounds through iodonium ion formation[7-11]. Similarly, at high anode potentials at platinum anode, perchloarates of lithium, sodium and quarternary ammonium salts, are reported to oxidise aromatic compounds [9].

EXPERIMENTAL

Materials

Acetonitrile (Merck) was employed as the solvent, which was purified as reported [12]. Benzaldehyde acetals were prepared using Dean-stark water trap, employing standard methods [13-14]. The acetals were preserved over freshly fused potassium carbonate. They were distilled under vacuum prior to use. The authenticity of the samples were confirmed by refractive index measurements and uv, ir and nmr spectral data. Tetraethyl ammonium perchlorate (Fluka AG) was used as such, as the supporting electrolyte.

Cell Assembly

Divided cell with G3 sinter, was employed. Platinum foils were used both as anode and cathode. In order to provide specific surface area, unwanted portions of the anode was insulated by waxing. The electrode surface was cleaned off organic impurities by washing with ethylene dichloride. The electrochemical oxidation was carried out galvanostatically using a DC power supply (Murphy). All the voltages of the working electrode were measured with reference to SCE using VTVM (Philips PP 9000)

Electro-Oxidation

A 0.05 M solutions of tetraethyl ammonium-perchlorate in acetonitrile was used both as anolyte and catholyte. 0.01 moles of respective acetals were introduced in the anolyte, which was kept stirred constantly using a magnetic stirrer. The calculated quantity of current was passed (Table 1)

After electrolysing, the anolyte was shaken with water to remove water soluble impurities

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TABLE 1

THE EXPERIMENTAL DETAILS OF ELECTROCHEMICAL OXIDATION OF ACETALS AT PLATINUM ELECTRODES.

Concentration of tetraethyl perchlorate	.. 0.05 M
Amount of Acetal	.. 0.010 M
Solvent	.. Acetonitrile
Temperature	.. 25 - 30° C
Surface area	.. 10.5 sq.cm
Electricity passed	.. 2.0 F./mole

S.No.	Potential Volt	Current density mA Cm^{-2}	% yield of ester* A	B	C
1	2	4.76	20	36	42
2	2.2	6.66	31	48	56
3	2.5	9.52	39	53	64
4	3	14.29	51	62	76

* A = Benzaldehyde di ethyl acetal
B = Benzaldehyde di n-butyl acetal
C = Benzldelyde di amyl acetal

The organic products mixture was separated by extraction with solvent ether. The products were separated in their pure states by column coupled with thin layer chromatographic techniques. The products were identified by Co-TLC, run with authentic samples and were confirmed spectroscopically using ir (Perkin Elmer 599 spectrometer) and HMR (Varian T-60).

The quantitative product distribution was determined with glc (Toshniwal).

Earlier, polarization studies were carriedout with solutions of the same concentration, in order to plot current potential curves.

RESULTS AND DISCUSSION

The polarization curves positively show the occurrance of oxidation under experimental conditions. (Fig.1)

All the acetals undergo oxidation at platinum anode, at comparatively higher potentials above the decomposition potential of the supporting electrolyte, Tetraethyl perchlorate (Viz. 1.6V vs SCE).

Some oxidized species in the medium which may be short lived can abstract the benzylic hydrogen from acetals. The resulting carbon radical II, may get anodically oxidised under the maintained potential, to produce the

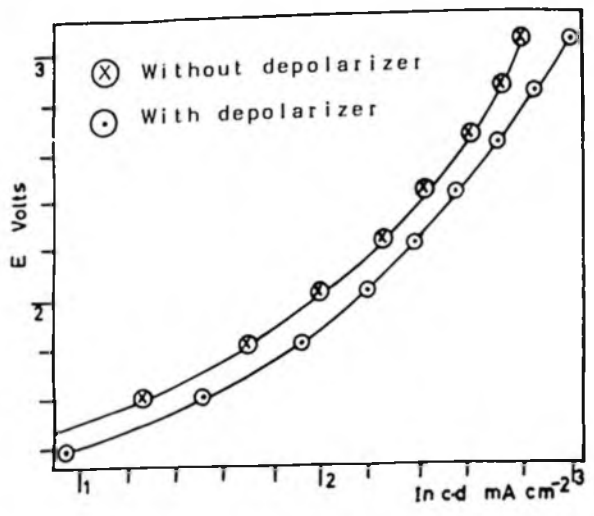
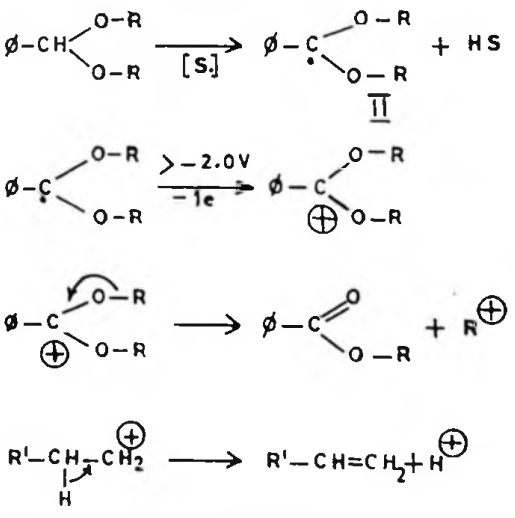


Fig. 1 Polarization curves

needed carbonium ion, which subsequently rearranges to the ester.

The probable mechanism for the electro chemical oxidation of acetal is proposed in Scheme 1.

Scheme :1.

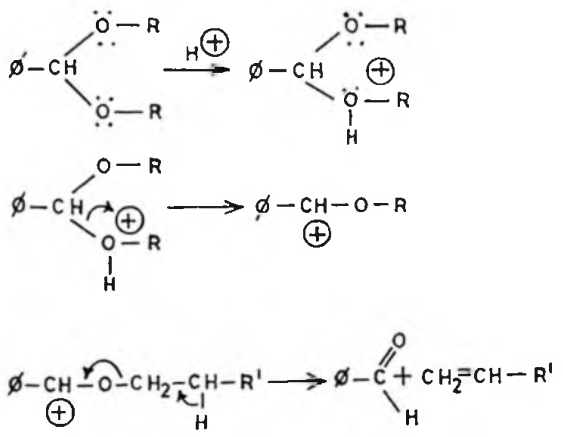


The involvement of the radical from the supporting electrolyte in the electrochemical reaction is evidenced by the fact that oxidation does not take place when the electrode potential is maintained below the decomposition potential of the supporting electrolyte as is normally done in electrochemical processes. In other words, esters are formed only when the potential is increased above the decomposition voltage of the medium. The decomposition potential of the

medium may not be sufficient to oxidize the substrate directly at the electrode, but some oxidized species in the medium may abstract the benzylic proton to yield the required carbonium ion. Below the decomposition potential, no oxidation occurs. This can be drawn from the fact that below 2.0 V no rearrangement is observed.

The $R^{\oplus}$ formed at the end of the reaction, may eliminate its proton, becomes olefin which is identified in glc. The traces of benzaedehyde formed in the product mixture may be attributed to the presence of protons which are rejected by $R^{\oplus}$ in solution. As the medium is strictly nonaqueous, only traces of benzaldehyde are observed. The probable route by which benzaldehyde would have resulted is explained in scheme 2.

Scheme : 2



The mechanism proposed is further evidenced from the observation that the yield of ester is found to increase as the alcohol fragment tends to be lengthier. This may be due to the increasing stability of $R^{\oplus}$ by the inductive influence of the longer carbon chain and due to the stability of the obefin, $R^{\oplus}$ is proposed to give.

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