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ELECTROOXIDATION OF ALKEN-1-YLARENES IN AQUEOUS ALCOHOL SOLUTIONS

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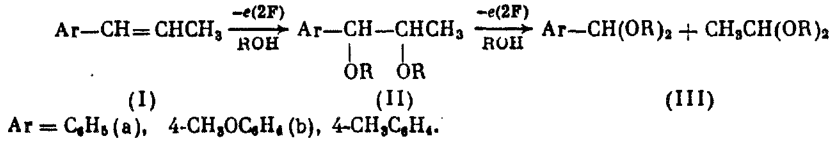
UDC 541.138.2:547.538.1

In the initial stages of the electrooxidation of alken-1-ylarenes — propenylbenzene (Ia) and 4-propenylanisole (Ib) — in aqueous alcohol solutions, 1,2-dialkoxypropyl- (II), 1-hydroxy-2-alkoxypropyl- (VII), and 1,2-dihydroxypropyl arenes (VIII) are formed. Subsequent rupture of the C—C benzyl bond converts the ethers (II) into benzaldehyde acetals (III) and benzaldehydes (IV), and compounds (VII) and (VIII) into (IV). Benzaldehydes (IV) are also formed from (II) by hydrolysis of the acetals (III) — partly for (IIIa) and completely for (IIIb). Electrolysis of (Ia and Ib) in aqueous alcohol solution leads mainly to their conversion into benzaldehydes (IV).

Electrooxidation of alken-1-ylarenes, for example, (I), in alcohol solution is an effective method for the preparation of benzaldehyde acetals [1, 2].



$$\underset{(I)}{Ar\text{—}CH\text{=}CHCH_3} \xrightarrow[ROH]{-e(2F)} \underset{(II)}{Ar\text{—}\underset{OR}{CH}\text{—}\underset{OR}{CH}CH_3} \xrightarrow[ROH]{-e(2F)} \underset{(III)}{Ar\text{—}CH(OR)_2} + CH_3CH(OR)_2$$

$Ar = C_6H_5$ (a), $4\text{-}CH_3OC_6H_4$ (b), $4\text{-}CH_3C_6H_4$.

We have established that in the presence of water conversion of the intermediates (II) is considerably reduced and instead of acetals (III) the main product of the process becomes benzaldehydes (IV) besides which, on passing electric current in excess of 4F per mole (I), alkyl benzoates (V) are formed.

$$\underset{(IV)}{Ar\text{—}CHO} \xleftarrow[ROH-H_2O]{4F} (I) \xrightarrow[ROH-H_2O]{>4F} \underset{(IV)}{Ar\text{—}CHO} + \underset{(V)}{ArCOOR}$$

Thus, whereas electrolysis of (Ib) (4F/mole) in anhydrous methanol yielded the acetal (IIIb) in 90% yield together with 5 mole % of unconverted (IIb) calculated on the initial (Ib), electrolysis in aqueous methanol (2.8 M water), other conditions being the same, resulted in an increase in unconverted (IIb) to 18% and the complete disappearance of the

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TABLE 1. Electrooxidation of Propenylbenzene (Ia) and 4-Propenylanisole (Ib) in Water—Alcohol Solutions[a]

Expt.	Alcohol	(Water) M	T, °C	Q, F/mole	Products of electrolysis of (I) and their yield, (mole/mole (I))·10^2				
					(II)	(III)	(IV)	(V)	(VII)
					Propenylbenzene (Ia)[b]				
1[c]	CH_3OH	0	55	8	5	47	–	–	–
2	»	5,6	55	8	10	16	5	–	11
3	»	11,2	55	8	19	8	3	–	15
4	»	11,2	55	10	13	7	10	10	14
5	»	0	55	2	61	–	–	–	–
6	»	11,2	55	2	37	–	<1	–	18
7	C_2H_5OH	0	75	8	3	44	–	–	–
8	»	2,2[d]	20	8	4	36	4	<1	<1
9	»	2,2[d]	75	8	4	16	13	<1	<1
					4-Propenylanisole (Ib)[b]				
10[c]	CH_3OH	0	55	4	5		–	–	–
11	»	2,8	55	4	18	–	53	–	–
12	»	5,6	55	4	23	–	12	10	11
13	»	11,2	55	4	14	–	19	6	12
14	»	0	55	2	68	14	–	–	–
15	»	5,6	55	2	32	<1	6	2	17
16	»	11,2	55	2	42	<1	9	–	20
17[c]	C_2H_5OH	0	75	4	15	58	–	–	–
18	»	2,2[d]	20	4	3	–	20	18	2
19	»	2,2[d]	75	4	5	–	44	5	3

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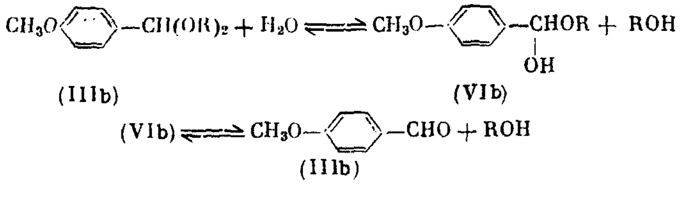
[a] Electrolysis was carried out in a cell without a diaphragm having a graphite anode and steel cathode, background electrolyte 0.2 M CF_3COONa, current density at anode 100-150 mA/cm^2.
[b] Conversion of (Ia, b): 95 (expt. 5), 66 (expt. 6), 89-96 (expts. 14-16), and 100% (remaining expts.).
[c] Results from [2].
[d] Rectified spirit, containing 4.4% water by wt.

acetal (IIIb), and the main product became the benzaldehyde (IVb) in 53% yield. On increasing the current passed to 5F/mole the ester (Vb) was formed in 5% yield, the amount of unconverted (IIb) was reduced to 3 mole % of (Ib), and the yield of (IVb) increased to 57%.

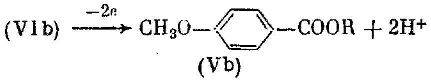
The object of the present work was to clarify the role of water in conversions of alkenylarenes in aqueous alcohol and in reducing the conversion of the intermediate (II).

To provide a solution to this question, an evaluation was carried out of the rate of hydrolysis of the acetals (IIa, b) and of the electrochemical conversion of the products of electrolysis of propenylbenzene (Ia) and 4-propenylanisole (Ib) in water—methanol and water—ethanol solutions on a background of sodium trifluoroacetate containing 2.8-11.2 M water (5-20% by volume) (Table 1).

Electrolysis of (Ia, b) was carried out under constant current conditions in a cell without a diaphragm using a graphite anode and a steel cathode at 20-75°C, current density 150 mA/cm^2, and total current passed = 4F/mole for (Ib) and 8F/mole for (Ia). The results obtained show that in the electrolysis of (Ib) water at a concentration of 2.8 M takes part largely in the hydrolysis of the acetal (IIIb) to hemiacetal (VIb) and benzaldehyde (IVb),



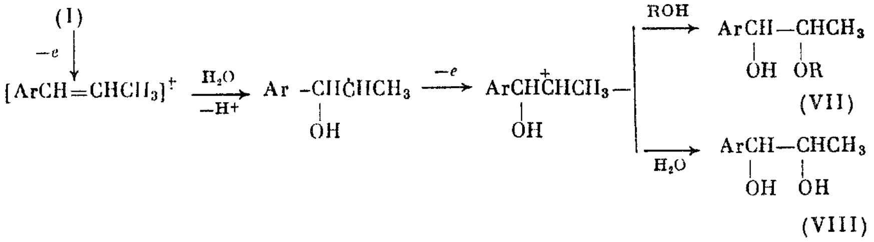
and we assume that the alkyl benzoate (Vb) is also formed via the hemiacetal (VIb)



Increasing the water content of the electrolyte and reducing the temperature favors the formation of the ester (Vb) (Table 1, experiments 12, 13, 18).

In the electrolysis of (Ia), because of the greater resistance of the benzaldehyde acetal (IIIa) to hydrolysis (Fig. 1) complete hydrolysis of the acetal formed does not occur, even with a water concentration of 11.2 M in the electrolyte. In this case, there is a marked reduction in the conversion of (IIa) and in the overall yield of benzaldehyde and its acetal as the water content is increased (Table 1, experiments 2-4, 8, and 9).

In addition to hydrolysis of the acetal, water, judging from the formation of 1-hydroxy-2-alkoxypropyl- (VII) and 1,2-dihydroxypropylarenes (VIII), participates in the electro-oxidative solvolysis of the cation radicals electrogenerated from (Ia, b).



As a result of subsequent electrochemical rupture of the benzyl C—C bond of (VII) and (VIII) these primary products of the electrolysis of (Ia, b) are converted into benzaldehydes (IV). In contrast to (VIIb), the glycol (VIIIb) does not accumulate in the course of the electrolysis (Fig. 2) which is evidence for a higher rate of its electrochemical conversion, comparable to the rate of the analogous conversions of (Ib). In this respect the ethers (II) and hemiethers (VII) are less reactive and because of this they accumulate in the electrolysate up to 90% conversion of (Ib).

Using the technique of concurrent reactions, we have established that the glycol (VIIIb) is 8 times more active at 55°C than the ether (IIb) (Fig. 3), and the latter is more active than the acetal (IIIb) and the aldehyde (IVb) by factors of 1.7 and 1.5, respectively (Table 2).

When the electrolysis of (I) is carried out in water—alcohol solutions, besides the complication of the electrochemical process a marked imbalance is observed between the amount of (I) reacted and the products (II)-(V) and (VII) which are formed (Table 1, experiments 10 and 11-13, 17, and 18-19) and this points to their active entrainment in side reactions. For example, one possibility is the hydrolytic conversion of arene cations, electrolytically generated from the aromatic compounds, into phenols; the latter are highly electroactive compounds which are readily oxidized in the electrolysis process to form resinous products. Benzaldehydes show a great tendency to electroreduction and it is suggested that this reaction too can be one of the secondary reactions. The participation of the electrolysis products of (I) in water-induced secondary reactions gives rise to an additional consumption of current and ultimately a fall in the efficiency of the electrochemical process, in particular, the conversion of the intermediates (II).

Thus, electrolysis of alkenylarenes in water—alcohol solutions is accompanied by rapid hydrolysis of the acetals (III) which are formed, and by active participation of water in the solvolysis of the electrochemically generated cation radicals. The increased activity of water in solvolysis, in comparison with methanol which has a comparable nucleophilicity [3] and a 2-10 times higher concentration in solution, leads one to suggest that solvolysis of cationic particles by water takes place mainly on the anode surface under the action of water molecules adsorbed thereon, these being retained more strongly than molecules of the alcohol.

EXPERIMENTAL

GLC analyses were carried out on a model 3700 chromatograph, with a flame ionization detector in a current of nitrogen (30 ml/min), equipped with stainless steel columns

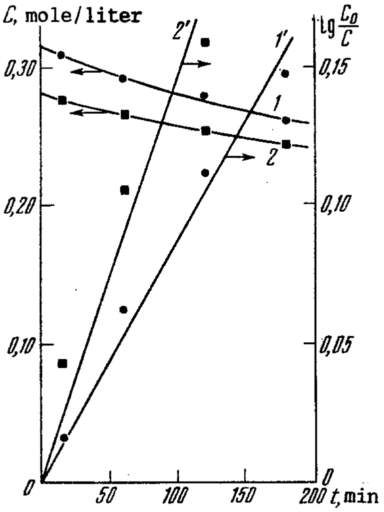


Fig. 1

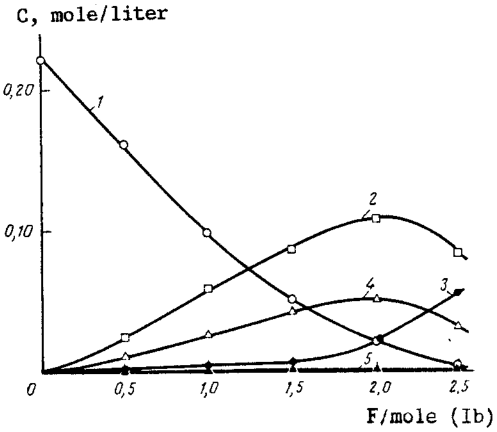


Fig. 2

Fig. 1. Kinetic curves of the hydrolysis of the dimethylacetals of benzaldehyde (IIIa) (1) and 4-methoxybenzaldehyde (IIIb) (2) in aqueous methanol at 55°C, and their plots on semilogarithmic coordinates (1' and 2'). Initial concentrations (M): water 5.6, (IIIa) 0.315, (IIIb) 0.282. Rate constants for the hydrolysis ($M^{-1} \cdot min^{-1}$): $(1.52 \pm 0.07) \cdot 10^{-4}$ for (IIIa) and $(4.43 \pm 0.02) \cdot 10^{-4}$ for (IIIb).

Fig. 2. Dynamics of the accumulation of electrooxidation products of 4-propenylanisole (Ib) (1) in aqueous methanol at 55°C: 2) diether (IIb), 3) aldehyde (IVb), 4) monoether (VIIb), 5) glycol (VIIIb).

TABLE 2. Relative Rate of Conversion of 4-(1,2-Dimethoxypropyl)anisole (IIb), 4-Methoxybenzaldehyde Dimethylacetal (IIIb) and 4-Methoxybenzaldehyde (IVb) in Concurrent Electrolysis with Benzaldehyde (IVa) in Methanol with a Sodium Trifluoroacetate Background at 55°C

Compound	(IVa)	(IIb)	(IIIb)	(IVb)
(IIb)	0,98	–	1,72	1,50
(IIIb)	0,52	0,58	–	0,86
(IVb)	0,60	0,67	1,16	–

(200 × 0.3 cm) packed with 5% OV 17 on Inertone Super (0.125-0.160 mm) and with 5% XE-60 on Chromatone N-AW (0.125-0.160 mm). PMR spectra of solutions in $CDCl_3$ were run on Jeol FQ 90Q (90 MHz) and Bruker M-250 (250 MHz) spectrometers, and mass spectra of the electrolysis products on Varian MAT-CH6 and MAT CH-111 (Gnom) instruments, the samples being introduced from the chromatograph.

Aqueous methanol solutions were prepared by the addition of water (5 to 20% by volume) to dry methanol. Sodium trifluoroacetate was "pure" reagent quality. Anodes were cylindrical bars of graphite of 8 mm diameter and cathodes 50 × 10 mm plates of stainless steel.

Propenylbenzene (Ia) was prepared from allylbenzene (a "pure" specimen) by boiling a solution in butanol in presence of KOH. 4-Propenylanisole (Ib) was the commercial product, isolated from fennel oil, redistilled in vacuum: bp 106-108°C/10 mm, n_D^{20} 1.5617 [4a], containing 98% of the main constituent. 4-(1,2-Dimethoxypropyl)anisole (IIb) was the product of electrooxidation of (Ib) in dry methanol [2]. Benzaldehyde (IVa) and 4-methoxybenzaldehyde (IVb) were "pure" reagents redistilled in vacuum. The acetals of these aldehydes were prepared by the method of [5]. 4-(1,2-Dihydroxypropyl)anisole (VIIIb), a 1:1 mixture of erythro and threo isomers, was the product of the alkaline hydrolysis of a mixture of erythro and threo isomers of 4-(1,2-diacetoxypropyl)anisole [6] purified by redistillation in vacuum and recrystallized from a mixture of hexane and chloroform.

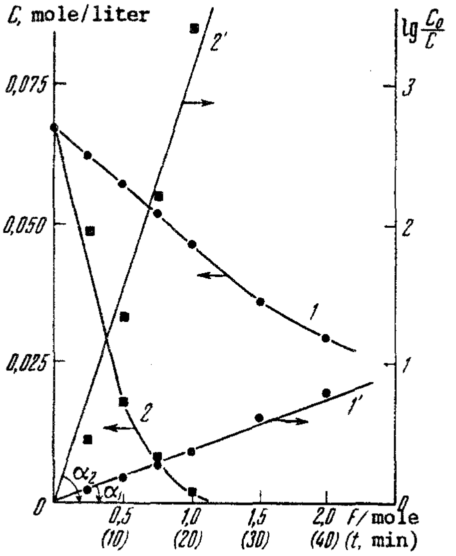


Fig. 3. Kinetic curves of the consumption of 4-(1,2-dimethoxypropyl)-anisole (IIb) (1) and 4-(1,2-dihydroxypropyl)anisole (VIIIb) (2) in concurrent electrooxidation in methanol at 55°C, and a semilogarithmic plot of these curves (1', 2').

PMR spectrum of (VIIIb) (δ, ppm): 1.02 and 1.08 d (3H, CH_3), 2.3-3.1 br. s (2H, OH), 3.80 s (3H, CH_3O), 3.82 and 3.95 m (1H, CHOH), 4.28 and 4.58 d (1H, CHC_6H_4), 6.87 and 7.25 m (4H, C_6H_4).

Electrooxidation of Propenylbenzene (Ia) and 4-Propenylanisole (Ib) in Aqueous Alcohol. General Method. The electrolysis was carried out at 20-75°C with a current of 0.3-0.6 A and a current density of 100-150 mA/cm² on the anode in a thermostatted cell of 30 ml capacity without a diaphragm. The cell was provided with a graphite anode, a steel cathode, a magnetic stirrer, thermometer, reflux condenser, and a dropping funnel. The cell was charged with 0.6 g (4 mmoles) CF_3COONa and 20 ml water—alcohol mixture with the required water content and a solution of 1.7 g (Ia) or 2 g (Ib) (13.2 mmoles in each case) in 10 ml of a water—alcohol mixture was placed in the dropping funnel and added dropwise during the 30 min electrolysis to the electrolyte present in the cell. The electrolysis was terminated after passing the quantity of electricity Q shown in Table 1. Alcohol and water were removed from the electrolyte on a rotary evaporator and the residue analyzed to determine the identity and yield of the electrolysis products using GLC, PMR spectroscopy, mass and chromatography-mass spectrometry and control and internal standards. The experimental results are set out in Table 1. The following products were isolated by distillation of the residue after evaporation in vacuum:

a) Benzaldehyde Dimethylacetal (IIIa). (R = CH_3) (Table 1, experiment 2), bp 100-104°C/13 mm, n_D^{20} 1.5095 [2]; PMR spectrum 3.33 s (6H, CH_3O), 5.45 s (1H, CH), 7.35 m (5H, C_6H_5); mass spectrum: 152 (M^+).

b) Benzaldehyde Diethylacetal (IIIa) (R = C_2H_5) (Table 1, experiment 8). bp 98-101°C/10 mm, n_D^{20} 1.4724 [4b]; PMR spectrum: 1.05 t (6H, CH_3), 3.39 m (4H, CH_2), 5.31 s (1H, CH), 7.20 m (5H, C_6H_5); mass spectrum: 180 (M^+).

c) 4-Methoxybenzaldehyde (IVb) (Table 1, experiment 10). A bp of 130-133°C/10 mm, n_D^{20} 1.5760 [4b]; PMR spectrum: 3.90 s (3H, CH_3O), 7.40 m (4H, C_6H_4), 9.87 s (1H, CH=O); mass spectrum: 136 (M^+); 2,4-dinitrophenylhydrazone, mp 254°C (xylene). Found (%): C 53.19, H 3.95, N 17.42. Calculated for $C_{14}H_{12}N_4O_4$ (%): C 53.16, H 3.79, N 17.73.

The remaining electrolysis products were identified without isolation: (IIa, b), (IIIb), (IVa), and (Va, b) by comparison with authentic specimens by GLC, and (VII) by chromatography-mass spectrometry. Chromatography-mass spectrum of (Vb): 196 (M^+, 5), 152(20), 151(100), 136(23), 135(35), 121(15).

Determination of the Rates of Hydrolysis of the Dimethylacetals of Benzaldehyde (IIIa) and 4-Methoxybenzaldehyde (IIIb) in Aqueous Methanol. A 3 ml freshly prepared 0.375 M solution of (IIIa) or 0.285 M (IIIb) in aqueous methanol containing 5.6 M water was stirred in a thermostat (55°C) in a tightly closed vessel and periodically sampled for determination of unchanged (III) by GLC using dodecane as internal standard. From the results obtained for the hydrolysis of (IIIa, b) the kinetics came under a pseudo-first order reaction for which, according to [7] (see Fig. 1): $k = (\log C_0/C)/[H_2O]\cdot t$.

Determination of the relative rates of the electrochemical conversions of 4-(1,2-dimethoxypropyl)- (IIb) and 4-(1,2-dihydroxypropyl)anisole (VIIIb) was carried out by the combined electrolysis of (IIb) and (VIIIb) in a 0.13 M methanol solution of CF_3COONa (30 ml), in the non-diaphragm cell described in the general method, at 55°C with initial concentrations of (IIb) and (VIIIb) $6.7\cdot10^{-2}$ M, current 0.3 A, current density at the anode 100 mA/cm^2. Unreacted (IIb) and (VIIIb) in the reaction mixture was determined using dodecane as internal standard. The results obtained (Fig. 3) show that the electrochemical conversion of (IIb) and (VIIIb) kinetically follows a pseudo-first order reaction. For such a reaction the ratio of the rates is proportional to the ratio of the tangents of the angles of slope of semilogarithmic plots of the kinetic curves of the consumption of the compounds concerned [7]. For the rates of the electrochemical conversion of (VIIIb) and (IIb), this ratio is 8.14.

The relative rates of the electrochemical conversions of (IIb), (IIIb), (IVa), and (IVb) (Table 2) were determined similarly by the combined electrolysis of (IIa), (IIIb), and (IVb) with (IVa) at 55°C, 0.125 A, current density at the anode 40 mA/cm^2 and initial concentration of the substrates $6.7\cdot10^{-2}$ M.

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