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ANODIC METHYLATION OF BENZALDEHYDE

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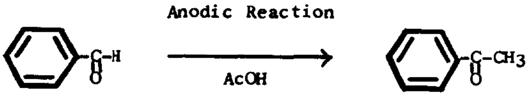
The anodic acetoxylation 1) and methylation 2) have been investigated with some substrates by several authors in the course of their studies of the electrochemical oxidation of acetic acid. However, no information on the anodic oxidation of aromatic aldehyde in aqueous acetic acid-potassium hydroxide solution has yet appeared in the literature. In this preliminary report we wish to describe a new type of anodic methylation, in which the hydrogen atom attached to the carbonyl of benzaldehyde is replaced by a methyl group giving acetophenone.



A mixed solution of benzaldehyde, acetic acid, water, methanol, and potassium hydroxide was electrolyzed at bright Pt electrodes ** for 36-56 hours at 25°, with a terminal voltage 10-15 V at a current of ca. 2 A, magnetically stirring, and changing the current direction in every 30 sec. by means of a commutator. Four typical reaction procedures (I, II, III, and IV) are shown in Table 1. The resulting alkaline solution was acidified with dilute sulfuric acid. The organic layer was separated by extraction with ether, washed with water, and then the reaction mixture was handled in the manner as shown in Scheme 1. Each fractions (A, B, C, and D, as shown in Table 2) were characterized by vapour phase and thin-layer chromatography and also by infrared spectra in comparison with those of authentic specimens. The Experiment IV (Table 3), reveals that the anodic methylation of benzaldehyde might occur more effectively, when electrolysis was carried out at higher current density and with more concentrated substrate.

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** The two platinum foil electrodes (1.5 X 2.0 cm^2) spaced about 2 mm apart.

TABLE 1

		Experiment			
		I	II	III	IV
PhCHO	(g)	21.2	10.6	10.6	10.6
AcOH	(g)	120	165	30 X 7	100 + 30 X 7
MeOH	(ml)	150	75	75	50
H_2O	(ml)	200	100	100	70
KOH	(g)	16.8	8.4	4.2	4.2
Time	(hrs.)	36	45	56	51
End Point	(pH)	7/8	6	4	4
Current	(A/cm^2)	0.6-0.77	0.7-1.0	0.7-1.0	0.9-1.0
PRODUCTS					
Neutral	(g)	14.44	10.0	11.0	11.0
Acidic	(g)	0.4	0.05	0.05	0.05

SCHEME 1

SEPARATION OF THE PRODUCTS

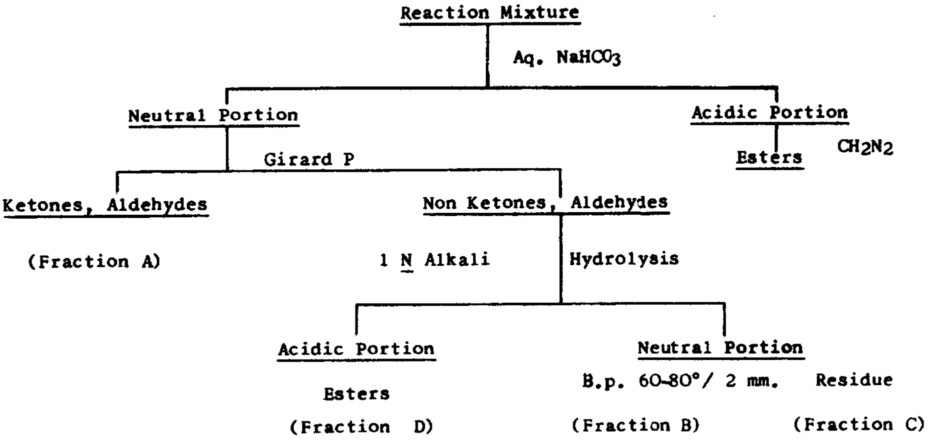


TABLE 2

Gas Chromatographic Data of the Products (Experiment I)

Fraction *	Constituent	Peak Area	(%)
A	Acetophenone	15.8	18.1
	p-Tolualdehyde	1.4	
	Methylacetophenones	0.6	
	Propiophenone	0.2	
	Others	0.1	
B	Benzyl Alcohol	36.4	37.0
	Methylphenylcarbinol	0.3	
	Others	0.3	
C	meso-Hydrobenzoin	19.6	33.5
	d,l-Hydrobenzoin	8.8	
	Dibenzyl Ether	0.3	
	Others	4.8	
D	Methyl Benzoate	11.0	11.4
	Methyl Toluates	0.3	
	Others	0.1	

* Separation of the each fractions was carried out by gas chromatography with a 45 m, 10% silicone oil coated Hitachi Golay column Z-45 (Se-30) operating at 140-200°.

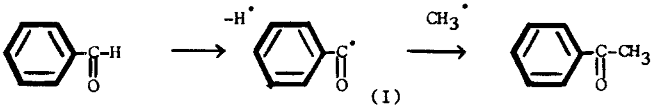
TABLE 3

Composition of the Products

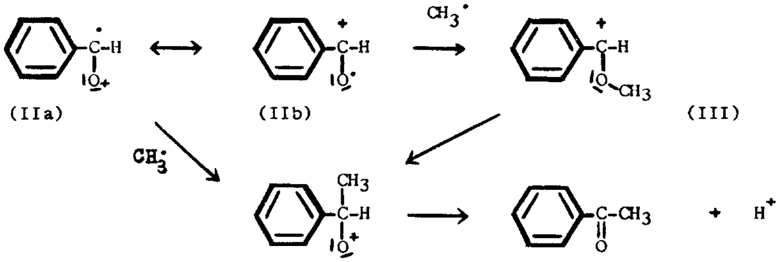
Fraction	Experiment I	II	III	IV
A	18.1	23.5	22.8	39.0
B	37.0	29.8	13.7	13.9
C	33.5	32.0	48.5	29.6
D	11.4	14.6	15.0	17.5

Since no significant precursor was isolated as seen in the results summarized in Table 2 except for about 0.3% amount of methylphenylcarbinol, acetophenone should have been produced directly from benzaldehyde in the present reaction. Thus, the following pathways may be considered as possible processes of the formation of acetophenone:

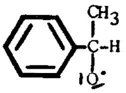
Path A: The abstraction of a hydrogen atom directly from the formyl group and/or from the benzene ring, by anodically generated radicals.



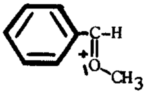
Path B: The formation of radical ion (IIa and IIb) by discharge of the substrate on the anode and addition of a methyl radical to give an intermediate (III), which may further undergo carbonium ion rearrangement to afford acetophenone.



Other pathways, e.g., the addition of methyl radical to the carbonyl of benzaldehyde may give IV, and electrophilic substitution of methyl carbonium ion may form V, are also considered.



(IV)



(V)

Benzoic acid and its derivatives may be derived from the intermediate IIb, which is affected with hydroxy anion to give the acids. meso- and d,l-Hydrobenzoins, and benzyl alcohol may be produced by the reduction of benzaldehyde $^{3)}$. The extension work of the anodic methylation to other derivatives of aromatic and aliphatic aldehydes is now in progress.

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