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The Anodic Reaction of Acetic Acid in the Presence of Enanthaldehyde, Enanthaldehyde Diethyl Acetal, and 2-Octanone

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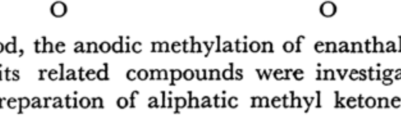
The anodic methylation of enanthaldehyde, enanthaldehyde diethyl acetal, and 2-octanone was attempted by electrolyzing a mixture of acetic acid, ethanol (or tetrahydrofuran and/or acetone), water, and potassium hydroxide. The major products from the electrolysis of enanthaldehyde consisted of 2-octanone, 1-heptanol, 3-methyl-2-octanone, and enanthaldehyde diethyl acetal. Similar products were isolated from the reaction mixture of enanthaldehyde diethyl acetal. The anodic methylation of 2-octanone gave 3-methyl-2-octanone as a major product. Possible mechanisms of the formation of these ketones were discussed.

Several workers[2-4] have reported the anodic methylation of aromatic rings, *i. e.*, trinitrotoluene and pyridine, and of double bond of 1,1-diphenylethylene. In the anodic methylation of benzaldehyde in aqueous acetic acid-potassium hydroxide solution,[5] we found the replacement of the hydrogen atom of the formyl group of benzaldehyde by a methyl group to give acetophenone. Such anodic methylation has been found to occur, recently, in the course of the electrolysis of the acetic acid solution containing cinnamic[6] and β-phenylglycidic acids.[7] As an extension of the above method, the anodic methylation of enanthaldehyde and its related compounds were investigated for the preparation of aliphatic methyl ketone.



$$\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}H} \xrightarrow[\mathrm{CH_3COOH}]{\text{Anodic Reaction}} \mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}CH_3}$$

Results and Discussion

Two platinum foil electrodes were used in the

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[2] F. D. Mango and W. A. Bonner, *J. Org. Chem.*, **29**, 1367 (1964).

[3] S. Goldschmidt and M. Minsinger, *Chem. Ber.*, **87**, 956 (1954).

[4] L. F. Fieser, R. C. Clapp and W. H. Daudt, *J. Am. Chem. Soc.*, **64**, 2052 (1942).

[5] A. Takeda, S. Torii and H. Oka, *Tetrahedron Letters*, **1968**, 1781.

[6] A. Takeda, S. Torii and H. Oka, *Memoirs of the School of Engineering, Okayama Univ.*, **3**, 107 (1968).

[7] A. Takeda, S. Wada, S. Torii and T. Takaki, unpublished work.

TABLE 1. REACTION PROCEDURES

Substrate (g)	n-$C_6H_{13}CHO$			n-$C_6H_{13}COCH_3$	n-$C_6H_{13}CH(OEt)_2$
	22.8	25	25	19.2	42 (98%)
CH_3COOH* (m*l*)	60+480[a)]	84+600[b)]	84+600[c)]	45+700[d)]	72+600[c)]
Org. Solvent	EtOH	THF	Me_2CO	EtOH	EtOH
(m*l*)	30	100	75	37.5	115
KOH (g)	8.0	8.4	8.4	6.3	8.4
H_2O (m*l*)	40	50	50	37.5	50.0
Reaction time (hr)	210	150	210	210	210
End point (pH)	3.5	3.5	4.0	3.5	4.0
Cell voltage (V)	14—16	16	14—16	14—16	15—16
Electric density (A/cm²)	0.4—0.6	0.7—0.8	0.33—0.43	0.43—0.80	0.43—0.80
Products					
Neutral (g)	6.5	10.6	12.7	8.6	15.0
Acidic (g)	0.2	0.3	0.7	0.3	0.4

* Additional acetic acid was added as follows: a) 60 m*l* every 26 hr, b) 50 m*l* every 12 hr, c) 50 m*l* every 16 hr, and d) 50 m*l* every 15 hr.

present experiments. Some typical reaction procedures are shown in Table 1. The products of the anodic reaction of enanthaldehyde and its related compounds were separated by chemical procedure into two groups as illustrated in Scheme 1. Both the ketone and aldehyde and the non-ketone and non-aldehyde components were characterized by vapor-phase gas chromatography (vpc). The principal products are summarized in Tables 2 and 3. 2-Octanone and its derivatives, which are expected to be produced from the anodic methylation of enanthaldehyde, were detected. By using the Girard P reagent, the ketone and aldehyde component was separated in about 50% yield. About 64% of the ketone and aldehyde component consisted of 2-octanone. The change of organic solvent had little effect on the constituent of the

TABLE 2. PRODUCTS OF ENANTHALDEHYDE

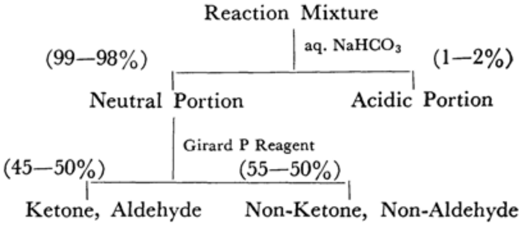
Constituent[a)]	Neutral portion Peak area (%)	Ketone and aldehyde Peak area (%)
Enanthaldehyde	3.70	6.56
2-Methylenanthaldehyde	0.43	0.78
2-Octanone	36.42	64.51
1-Heptanol	25.81	—
3-Methyl-2-octanone	12.96	22.56
3-Nonanone	1.46	2.59
Enanthaldehyde diethyl acetal	5.65	—
n-Heptyl acetate	4.16	—
Others	9.37 (8 peaks)	4.43 (4 peaks)

a) Separation of the each constituent was carried out by gas chromatography with a 45 m, 10% silicone oil coated Hitachi Golay column Z-45 (SE-30) operating at 75 and 90°C.

TABLE 3. PRODUCTS OF 2-OCTANONE AND ENANTHALDEHYDE DIETHYLACETAL

Constituent[a)]	Substrate (peak area, %) n-$C_6H_{13}CH(OEt)_2$	n-$C_6H_{13}COCH_3$
Enanthaldehyde	2.13	—
2-Octanone	28.83	54.60
2-Octanol	—	2.80
3-Methyl-2-octanone	4.65	32.30
3-Nonanone	0.24	2.46
Enanthaldehyde diethyl acetal	14.23	—
2-Octanone diethyl ketal	—	6.45
Others	46.62	1.39

a) Separation was carried out with Hitachi Golay column Z-45 operating at 90°C.



Scheme 1. Separation of the products.

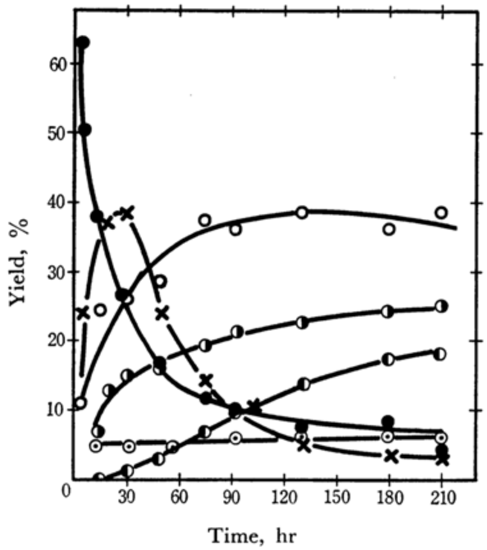


Fig. 1. Relationship between reaction time and yield of constituents in the electrolysis of enanthaldehyde.

● Enanthaldehyde, ○ 2-octanone,
◑ 1-heptanol, ◐ 3-methyl-2-octanone,
⊙ enanthaldehyde diethyl acetal,
× enanthaldehyde ethyl hemiacetal (vpc characterized).

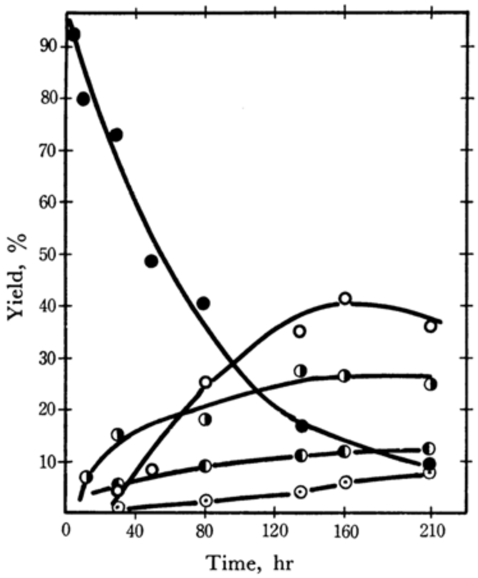


Fig. 2. Relationship between reaction time and yield of constituents in the electrolysis of enanthaldehyde diethyl acetal.

● Enanthaldehyde ethyl hemiacetal,
○ 2-octanone,
◑ enanthaldehyde,
◐ enanthaldehyde diethyl acetal,
⊙ 3-methyl-2-octanone.

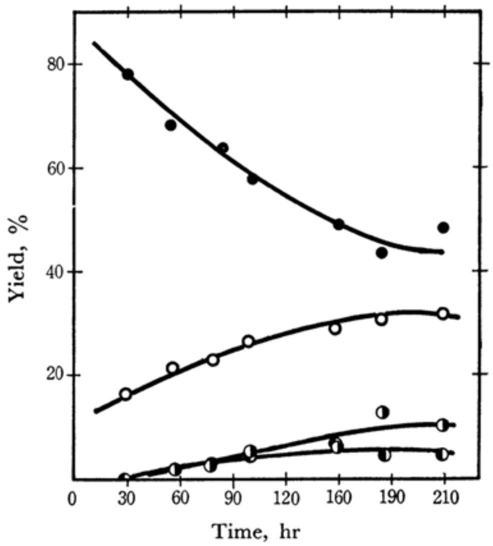


Fig. 3. Relationship between reaction time and yield of constituents in the electrolysis of 2-octanone.

● 2-Octanone,
○ 3-methyl-2-octanone,
◑ 2-octanone diethyl ketal,
◐ 3-nonanone.

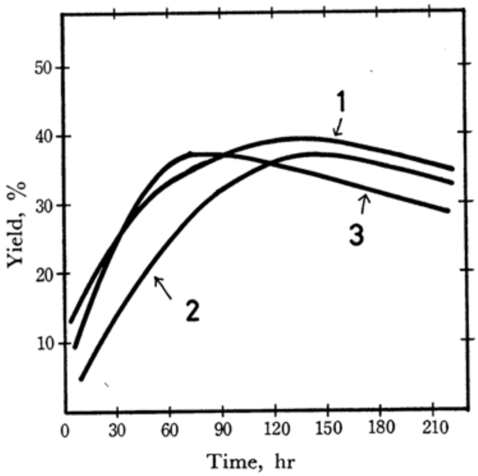


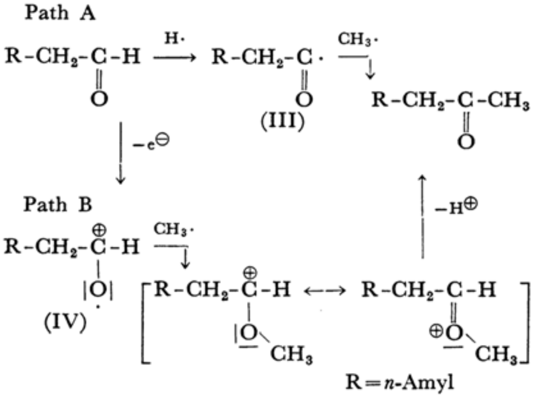
Fig. 4. Relationship between reaction time and yield of 2-octanone, using various solvents.

1 Ethanol, 2 tetrahydrofuran, 3 acetone.

products.

When anodic methylation was carried out in the presence of enanthaldehyde diethyl acetal as a substrate, the constituent of the major products was similar to that described in Table 2. The anodic methylation of 2-octanone afforded 3-methyl-2-octanone as a major product. The results of each reaction which was carried out for 210 hr are illustrated in Figs. 1, 2, and 3. The results of the formation of 2-octanone in different solvents are shown in Fig. 4.

The results given in Fig. 1 show that the methylation and the reduction of enanthaldehyde proceed principally to afford 2-octanone and 1-heptanol. In the course of this reaction, some enanthaldehyde may be converted into its hemiacetal and diethyl acetal. By electrolyzing 2-octanone in the same media, 3-methyl-2-octanone was produced (Fig. 3). The maximum yield of 2-octanone, in Fig. 1, was estimated when electrolysis was continued for about 140 hr. The line attributed to enanthaldehyde hemiacetal in Fig. 2 shows that the conversion of enanthaldehyde diethyl acetal into the hemiacetal may be performed for a relatively short period. In Fig. 4, it seems that the organic solvent used in the present reaction affected only the rate of the formation of 2-octanone.

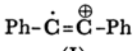


Scheme 2. Formation of 2-octanone.

Path A: The abstraction of a hydrogen atom directly from the formyl group by anodically generated radicals.

Path B: The formation of radical ion (IV) by discharge of the substrate on the anode and the addition of a methyl radical followed by carbonium ion rearrangement.

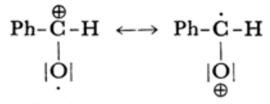
Recently, Koehl hypothesized[8] that a cation-radical intermediate (I) may be produced, when the triple bond of diphenylacetylene was subjected to discharge at the anode surface. In a previous paper,[5] we also assumed a possibility in which



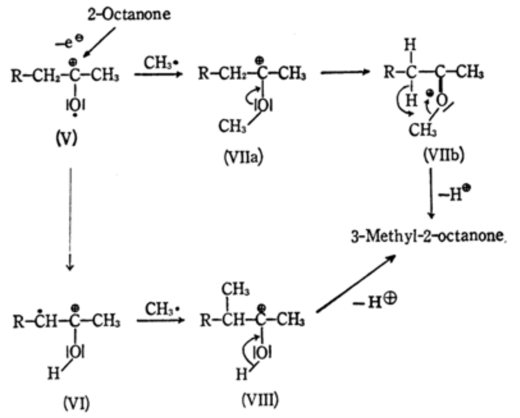
$$\mathrm{Ph\text{-}\dot{C}{=}\overset{\oplus}{C}\text{-}Ph}$$

(I)

discharge of the carbonyl group of benzaldehyde at the anode may give cation radical intermediate (IIa and IIb), since no appreciable amount of benzil was detected on the gas chromatogram. Similarly, in the case of enanthaldehyde, absence of dimer of heptanoyl radical (III) was confirmed by vpc. A possible pathway of the formation of 2-octanone may be considered as follows (Scheme 2):



(IIa) (IIb)



Scheme 3. Formation of 3-methyl-2-octanone.

However, considering the mode of attack of a methyl radical to 2-octanone, the assumption of the cation-radical intermediate (IV) seems to be more reasonable. A mechanism of the formation of 3-methyl-2-octanone *via* radical-cation intermediates is outlined in Scheme 3. Considering the facility of the formation of 3-methyl-2-octanone rather than 3-nonanone, it seems that the anodically generated methyl radical[9] may attack radical-cation intermediates (V and VI) to form (VII and VIII), which may further undergo carbonium ion rearrangement giving 3-methyl-2-octanone.

Experimental

All boiling points are uncorrected. The products were analyzed by vapor-phase chromatography (Hitachi F6-D gas chromatograph) using Golay column (Z-45) coated with silicone oil (SE-30).

Apparatus. The electrochemical cell consisted of a cylindrical glass vessel, 7 cm long in diameter and 14 cm high, fitted with a gas lead pipe, a thermometer, and a magnetic stirrer. The vessel was immersed in a water bath, cooled with circulating cold water. The electrodes were two platinum foils ($1.5\times2.0\ \mathrm{cm^2}$) spaced about 2 mm apart and the current direction was changed every 30 sec by means of a commutator.

Materials. Analytical grade enanthaldehyde, 2-octanone, acetic acid, ethanol, tetrahydrofuran, acetone, and inorganic chemicals were used. The following reference compounds were prepared: enanthaldehyde diethyl acetal,[10] bp 99—102°C/25 mmHg, α-methyl-

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enanthaldehyde,[11] bp 50—52°C/10 mmHg, 3-methyl-2-octanone,[12] bp 64°C/18 mmHg, 3-nonanone,[13] bp 85—88°C/20 mmHg, 1-heptanol,[14] bp 71—72°C/12 mmHg, 1-heptyl acetate,[15] bp 192°C.

General Procedure. A typical reaction procedure is shown in Table 1. A mixed solution of the substrate, acetic acid, water, the organic solvent, and potassium hydroxide was electrolyzed at Pt electrodes for about 210 hr at 25—35°C, with terminal voltage 14—16 V at a current of 1.2—2.4 A, magnetically stirring, and changing the current direction every 30 sec by means of a commutator. The resulting reaction mixture was diluted with 300 m*l* of water and extracted with ether. The extracts were washed with a saturated aqueous sodium chloride solution and concentrated *in vacuo*. The separation of the products was carried out in the manner shown in Scheme 1. The results of gas chromatography of each experiment are indicated in Tables 2 and 3. The isolation of enanthaldehyde ethyl hemiacetal from the non-ketone and non-aldehyde components through distillation failed. However, we succeeded in detecting the hemiacetal in the high-boiling fraction of the non-ketone and non-aldehyde components both spectroscopically and gas chromatographically: IR (cm^{-1}) 3500—3200 (OH) and 1120—1040 (hemiacetal); vpc with a 1 m, 10% silicone oil (SE-30) coated Chromosorb W (NAW) column operating at 140°C and 0.4 kg/cm^2 (N_2): Retention time 18 min.

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