The Anodic Oxidation of Esters

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A previous work$^{1)}$ in this series dealt with the electrochemical coupling reaction of diethyl malonate and ethyl acetoacetate in absolute alcohol. Although the desired products were obtained in a small yield, they were contaminated with many by-products which were formed by the electrolysis of the alcohol itself. It has also been concluded that the solvent might play an important role in this reaction.

Therefore, as a new attempt, the present work was carried out for the purposes of obtaining a better yield of the dimer of esters in the electrolysis and of controlling the side reaction by using acetonitrile as a solvent, with no active hydrogen, and, as a supporting electrolyte, a potassium iodide which gave a better conductivity than the sodium salt of esters in the same solvent.$^{2)}$

The dimerization of esters is a novel method not only because of the electrolysis but also because of the chemical synthetic method.

In order to make a comparison with the case of an absolute alcohol, a malonic ester,

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1) T. Okubo and S. Tsutsumi, *Tec. Rep. Osaka Univ.* **13**, 495 (1963).

2) E. White, *J. Chem. Soc.*, **1928**, 1414. (Although the data are for conductivities in an alcohol solution, this statement is also true for an acetonitrile solution in our blank test.)

an acetoacetic ester and a phenylacetic ester were used in this experiment.

Results and Discussion

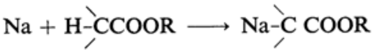
The yield of a coupling product was calculated on the basis of the amount of product per unit qantity of electricity.

The experimental results are summarized in Table I.

As is shown in the table, the modified method in which acetonitrile was used as a solvent afforded more satisfactory results in all cases.

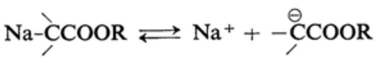
The Electrochemical Coupling of Esters in an Alcoholic Solution.—According to the explanation proposed by Allen,[3] the electrolytic coupling of these esters in an alcoholic solution proceeds in a manner similar to that of the Kolbe reaction, with the exception that no carbon dioxide is eliminated, as is shown below.

Step 1) The metallation of the ester (The formation of the anion of the ester)



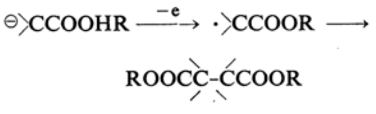
$$Na + H\text{-}CCOOR \longrightarrow Na\text{-}C\,COOR$$

Step 2) The dissociation of the alkali salt of the ester



$$Na\text{-}CCOOR \rightleftarrows Na^+ + -\overset{\ominus}{C}COOR$$

Step 3) The anodic oxidation of the anion



$$\ominus\rangle CCOOHR \xrightarrow{-e} \cdot\rangle CCOOR \longrightarrow ROOCC\text{-}CCOOR$$

For the electrolysis in an alcoholic solution, it was observed that the reactivity of the ester toward the electrolytic coupling was dependent on the electron-attracting force of the substituents on the methyl group (CH_3) of ethyl acetate ($CH_3COOC_2H_5$). The decrease in the reactivity of the ester caused by the substituent was in the order; carbethoxy $COOC_2H_5$, acetyl CH_3CO and phenyl C_6H_5. The order was just the same as Taft's substituent constants[4] for CH_2X–, as is shown below.

$$C_6H_5,\ +0.215 < CH_3CO,\ +0.60 < COOC_2H_5,\ +0.7$$

On the reaction of ethyl acetoacetate and ethyl phenylacetate in alcohol, because their releasing force of hydrogen is lower than that of ethyl malonate, the yield of coupling products was very poor (ethyl acetoacetate, 0.2 g./amp. hr.; ethyl phenylacetate, a trace, and by the following reaction, acetoaldehyde and its polymeric material were the main products;

$$C_2H_5\overset{\ominus}{O}: \longrightarrow C_2H_5O\cdot + e$$

$$C_2H_5O\cdot \longrightarrow CH_3CHO + 1/2\ H_2$$

The Electrochemical Coupling of Esters in an Acetonitrile Solution.—When these esters were submitted to electrolysis in a potassium iodide-acetonitrile medium, the dimer of esters was yielded, especially in the cases of both ethyl acetoacetate and ethyl phenylacetate. The dimer which could not hitherto be isolated as a crystal in the case of an alcoholic solution was obtained as a fine crystal and in a good yield.

The reasons for this may be as follows:

1) An acetonitrile was scarcely oxidized in

TABLE I. SUMMARY OF THE RESULTS

Ester	Product In absolute alcohol	Product In acetonitrile
Diethyl malonate	$HC(COOC_2H_5)_2$ | $HC(COOC_2H_5)_2$ (1.4 g./amp. hr.)	$HC(COOC_2H_5)_2$ | $HC(COOC_2H_5)_2$ (2.1 g./amp. hr.) (0.013 mol./amp. hr.)
Ethyl acetoacetate	(1) $CH_3COCH(COOC_2H_5)$ | $CH_3COCH(COOC_2H_5)$ (identified as acetonylacetone) (0.2 g./amp. hr.) (2) CH_3CHO and polymeric materials	$CH_3COCH(COOC_2H_5)$ | $CH_3COCH(COOC_2H_5)$ (1.5 g./amp. hr.) (0.0115 mol./amp. hr.)
Ethyl phenylacetate	(1) $C_6H_5CH(COOC_2H_5)$ | $C_6H_5CH(COOC_2H_5)$ (trace) (2) CH_3CHO and polymeric meterials	(1) $C_6H_5CH(COOC_2H_5)$ | $C_6H_5CH(COOC_2H_5)$ (2.3 g./amp. hr.) (0.014 mol./amp. hr.) (2) a small amount of a tarry product

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[3] M. J. Allen, "Organic Electrode Processes," Reinhold Pub. Corp., New York (1958), p. 111.

[4] M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, New York (1956), p. 595.

the anodic oxidation as compared with an alcohol, and the amounts of by-products are small.

2) The dissociation of the potassium salt of the ester is easier than that of sodium salt.

3) The velocity of the reaction was accelerated by the action of the iodide formed, as is shown in the reaction path.

The yield of coupling products indicated in (mol./amp. hr.) was nearly constant in each case. It is noticeable that the difference in the acidity between esters is not very important in the reactions in acetonitrile because the acidities of the esters used are much stronger than that of acetonitrile.[5]

The following reaction path may be inferred.

$$KI \longrightarrow K^+ + I^- \qquad (1)$$

$$K^+ \xrightarrow{+e} K\cdot \qquad (2)$$

$$I^- \xrightarrow{-e} I\cdot \qquad (3)$$

$$K\cdot + RCH_2COOC_2H_5 \longrightarrow RC(K)HCOOC_2H_5 + 1/2\ H_2 \qquad (4)$$

$$RCH(K)COOC_2H_5 \longrightarrow R\bar{C}HCOOC_2H_5 + K^+ \qquad (5)$$

$$R\bar{C}HCOOC_2H_5 \xrightarrow{-e} R\dot{C}HCOOC_2H_5 \qquad (6)$$

$$2R\dot{C}HCOOC_2H_5 \longrightarrow \begin{array}{l} RCHCOOC_2H_5 \\ \quad | \\ RCHCOOC_2H_5 \end{array} \qquad (7)$$

$$I\cdot + RC(K)HCOOC_2H_5 \longrightarrow KI + R\dot{C}HCOOC_2H_5 \qquad (8)$$

$$R = C_6H_5,\ COOC_2H_5,\ CH_3CO$$

Experimental*

Materials.—*Acetonitrile.*—Commercial grade acetonitrile was carefully purified in the usual manner. (B. p. 81.0°C, n_D^{20} 1.3440).

Ethyl Malonate and Ethyl Acetoacetate (commercial grade) were fractionated. (Ethyl malonate: b. p. 197∼198°C, n_D^{18} 1.4120; Ethyl acetoacetate: b. p. 89∼90°C/30 mmHg, n_D^{20} 1.4190) Ethyl phenylacetate was prepared by the method given in the literature[6] (115∼117°C/20 mmHg, n_D^{23} 1.4959).

Apparatus.—Electrolyses were carried out in a cylindrical glass vessel fitted with a reflux condenser and two platinum foil electrodes with an area of $20 \times 30\ mm^2$ and spaced 5 mm. apart. During the coures of the electrolysis, the contents were stirred magnetically and the temperature was controlled by a water bath.

The Electrolysis of Ethyl Malonate in Acetonitril Containing Potassium Iodide.—A solution of 30 g. of ethyl malonate and 0.5 g. of potassium iodide in 100 ml. of acetonitrile was electrolyzed at 10°C for 36 hr. A current was maintained at 0.2 amp. After the removal of the acetonitrile, the electrolyte solution was poured into cold water and extracted with ether. The ethereal layer was then washed with water and dried over anhydrous magnesium sulfate, and the ether was removed. The remaining oil was distilled under reduced pressure. The fraction with a b. p. of 180∼187°C/12 mmHg was 15 g. After recrystallization from alcohol, they afforded tetraethyl ethanetetracarboxylate (m. p. 74∼75°C), and the melting point was undepressed on admixture with an authentic sample.[7] Moreover the infrared spectrum of this compound was identical with that of an authentic sample.

The Electrolysis of Ethyl Acetoacetate in Acetonitrile Containing Potassium Iodide. — A mixture of 30 g. of ethyl acetoacetate, 0.5 g. of potassium iodide, and 100 ml. of acetonitrile was electrolyzed at 10°C for 27 hr. During the electrolysis, a current was maintained at 0.3 amp. After the removal of the acetonitrile, the residue was vigorously shaken with cold water and a solid was separated by filtration. When the solid was then washed with water and dried in vacuo, the yield was 12 g. It was then recrystallized from alcohol (m. p. 81∼83°C). The recrystallization of this crystal from aqueous alcohol gave the β-form of diethyl diacetosuccinate* (m. p. 86.5∼88°C). The melting point of this compound was not depressed on admixture with an authentic sample prepared according to the directions of Knorr and Haber.[8] The infrared spectra of the compound were identical with those of an authentic sample.

Found: C, 55.72; H, 6.83. Calcd. for $C_{12}H_{18}O_6$: C, 55.81; H, 6.97%.

The Electrolysis of Ethyl Phenylacetate in Acetonitrile Containing Potassium Iodide. — The experiment was conducted in a manner essentially similar to that of the experiment described above. The solid (m. p. 128∼135°C) (3.5 g.) was suspended between aqueous and ethereal layers, and the residue (14 g.) was obtained from an ethereal layer. The solids were combined and submitted to sublimation. The sublimated crystals were extracted with hot petroleum ether (b. p. 40∼55°C) to remove low melting parts. The remaining crystals were recrystallized from alcohol, melted at 138.5∼140°C and identified as ethyl β-diphenyl-succinate[9] by mixed melting point measurement.

Found: C, 73.27; H, 6.62. Calcd. for $C_{20}H_{22}O_4$: C, 73.61; H, 6.74%.

A trace of unidentified crystals (m. p. 77∼81°C) was obtained from the hot petroleum ether-soluble part.

The Electrolysis of the Sodium Salt of Ethyl Phenylacetate in Absolute Alcohol.—To a solution of 25 g. of ethyl phenylacetate in 100 ml. of absolute alcohol, 0.5 g. of sodium was added, and then the

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[5] D. J. Cram, "Organic Chemistry," McGraw-Hill Book Co., New York (1959), pp. 172, 176.

* Melting points and boiling points are uncorrected.

[6] "Organic Syntheses," Coll. Vol. I (1948), p. 270.

[7] C. A. Bischoff, *Ber.*, **17**, 2781 (1884).

* Diethyl diacetosuccinate has many tautomers. Among them are the β-form (diketo form) and the γ-form (diketo form). Their melting points are 89∼90°C (plate form) and 74°C (needle form) respectively. In the presence of water, the γ-form is transformed into the β-form.

[8] L. Knorr and F. Haber, ibid., **27**, 1155 (1894).

[9] H. Wren and C. J. Still, *J. Chem. Soc.*, **1915**, 444.

solution was subjected to electrolysis. The electrolysis was carried out at an average current of 0.2 amp. at 20°C for 30 hr. The precipitate (2 g.) was separated by filtration. This precipitate was dissolved in water, acidified with dilute hydrochloric acid, and then extracted with ether. After the removal of the ether, a trace of crude crystals was obtained; when sublimated, it yielded ethyl β-diphenylsuccinate (m. p. 120∼135°C). An attempt to purify this compound was unsuccessful. After the evaporation of the alcohol, the filtrate was distilled under reduced pressure to give the following fractions.:

Fraction 1: 100∼118°C/20 mmHg 17.8 g. (unchanged ester)
Fraction 2: 40∼80°C/3 mmHg
Fraction 3: 80∼85°C/3 mmHg 1 g. n_D^{24} 1.496
Fraction 4: 100∼110°C/3 mmHg 0.9 g. n_D^{24} 1.500
Fraction 5: 115∼130°C/3 mmHg 0.9 g. n_D^{24} 1.558

Fraction 2 was converted into its 2,4-dinitrophenylhydrazone (m. p. 230∼233°C (recrystallized from a mixture of alcohol and nitrobenzene)). As the I. R. of this hydrazone showed no C=O band, the fraction seems not to be an ester and aldehyde polymer resulting from the electolysis of alcohol. Fractions 3, 4, and 5 were soluble in both ether and alcohol, and the I. R. of these fractions showed the characteristic absorption bands of the ester.

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