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Selective Kolbe Electrolytic Coupling Using Glasslike-Hard Carbon Anodes

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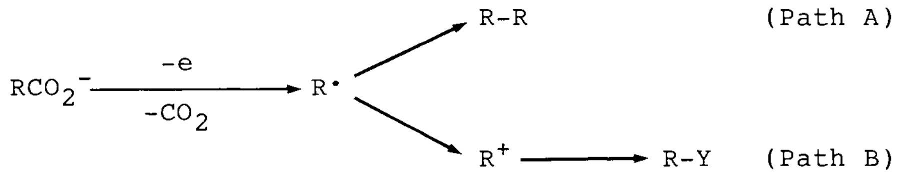
The use of some kinds of glasslike-hard carbons was found to lead to selective synthesis of the corresponding Kolbe coupled products in high yields comparable to the use of a Pt anode in anodic oxidation of some carboxylic acids.

Anodic oxidation of carboxylic acids has been well studied because of its mechanistic interests and the usefulness in organic synthesis.[1] Commonly shown in the Kolbe electrosynthesis, the coupling products R-R are formed via an anodically generated radical R$^\bullet$ from carboxylates ions RCO_2^- (Path A, Eq.1). However, in certain cases (Hofer-Moest reaction) other products, such as alcohols, esters, ethers are obtained via a carbenium ion R^+ generated by further oxidation of the radical R$^\bullet$ (Path B, Eq.1).



(1)

Whether the reaction proceeds via the radical or the ionic process depends on some factors, e.g. solvent, current density, pH, electrolyte and anode materials. It is especially well known that the effect of anode material is remarkable on the product composition in Kolbe reaction.[2] For example, with carbon anodes the predominant products are usually derived from carbenium ions whereas the use of a smooth platinum can lead to preferential formation of radical coupled products.[3,4] Kolbe electrolytic couplings are industrially important for syntheses of useful chemicals such as an intermediate of synthetic fibers,[5] a plant growth stimulator[6] and pheromones[7] although the reaction requires the use of Pt or Pt/Ti electrode. Platinum is too expensive for industrial uses and is found to be diminished during electrolysis of organic compounds[8] and Pt/Ti electrode is substituted for Pt electrode. However, it is unstable and suffers corrosion under the condition of electrolysis in the presence of organic substance. Toughness for organic solvents and easy availability of carbon materials have tempted us to investigate the correlation between the materials of electrodes and the natures of Kolbe reaction.

We investigated the anodic oxidation of phenylacetic acid using some kinds of carbon electrodes as an anode. We used methanol/pyridine as a solvent and electrolysis was performed at a constant current in an undivided cell.[9)] The results were tabulated in Table 1. Benzyl methyl ether **1**, benzyl alcohol **2** and methyl phenylacetate **3** were formed via an ionic process, and dibenzyl **5** was formed via a radical process. The isolated yields and the ratio of radical-derived products/cationic-derived products are given in the Table. In the same manner as Ross's report,[4)] none of radical coupled products was produced with a carbon anode[10)] although the use of a Pt anode can lead to predominant formation of a radical-coupled product. At first, we attempted the surface modification of carbon to prepare a gold sputtered carbon[11)] and a diamond-like-carbon coated carbon,[12)] and then carried the electrolysis using them as an anode (runs 3, 4, 5). This attempt made it possible to promote the formation of radical-coupled products with a carbon anode. However, it was found to be insufficient because some parts of the modification surface peeled off during the electrolysis.

$$\underset{\mathbf{4}}{PhCH_2CO_2H} \xrightarrow{-e} \underset{\mathbf{1}}{PhCH_2OCH_3} + \underset{\mathbf{2}}{PhCH_2OH} + \underset{\mathbf{3}}{PhCH_2CO_2CH_3} + \underset{\mathbf{5}}{PhCH_2CH_2Ph}$$

Table 1. Anodic Oxidation of Phenylacetic acid with Some Carbon Type Anodes[a)]

		Yield of products/%				
Run	Anode	**1**	**2**	**3**	**5**	**5/1+2+3**
1	Carbon	40(41)[b)]	4(6)[b)]	3(5)[b)]	0(0)[b)]	0(0)[b)]
2	Pt	18(14)[b)]	6(4)[b)]	4(4)[b)]	45(32)[b)]	1.61(1.78)[b)]
3	Carbon(Au)	43	3	1	5	0.11
4	GC-B(Au)	44	6	3	14	0.26
5	Carbon(DLC)	44	3	2	10	0.20
6	GC-A[c)]	26	6	2	40	1.18
7	GC-B[c)]	43	6	4	0	0
8	GC-C[c)]	44	6	4	0	0
9	GC-D[c)]	31	4	3	24	0.63
10	GC-E[d)]	18	4	3	48	1.92
11	GC-F[d)]	32	6	4	43	1.02
12	GC-G[d)]	38	8	2	32	0.67

a) CH_3OH/Py(4/1), Na(0.043 equiv.), 2 F/mol, 20 °C. b) Reported result of Ross et al.[4)] c) Showa Denko Co., Ltd.; Graphite powder is added to GC-B and GC-C in manufacturing process. d) Tokai Carbon Co., Ltd.

Table 2. Properties of Glasslike-Hard Carbons

	Bulk density $g\ cm^{-3}$	Apparent porosity %	Gas permeability $cm^2\ s^{-1}$	Shore hardness	Electrical resistivity $10^{-4}\ \Omega\ cm$
GC-A	1.55	-	$<10^{-6}$	-	47
GC-C	1.50	-	$<10^{-6}$	-	42
GC-D	1.60	-	$<10^{-5}$	-	26
GC-E	1.48—1.51	0.2—0.4	10^{-11}—10^{-12}	110—120	45—50
GC-F	1.47—1.50	1 — 3	10^{-10}—10^{-12}	100—110	40—45
GC-G	1.44—1.47	3 — 5	10^{-7} —10^{-9}	70— 80	35—40

Next, we tried some glasslike-hard carbons which were manufactured by solid phase carbonizations and had three dimensional bond structure in contrast to two dimensional bond structure of soft carbon like a commercial graphite. Product distribution of this electrolysis was largely influenced by the nature of glasslike-hard carbons. It is especially noteworthy that GC-E(run 10) and GC-A(run 6) were as effective as Pt in promoting the formation of Kolbe dimer. Since the results with phenylacetic acid **4** showed that the two glasslike-hard carbon electrodes gave comparable yields of Kolbe dimer to Pt, further study was extended to some carboxylic acids. These results were tabulated in Table 3. Again comparable amounts of the Kolbe dimers are formed at GC-E and GC-A electrodes. Although Brettle et al. reported the use of vitreous carbon and baked carbon (some kinds of hard carbon) led to substantial yields of Kolbe dimer,13) yields of our present electrolysis were much better than that of Brettle's and comparable to that of Pt. Consequently, GC-E and GC-A are found to be very promising materials as an anode of Kolbe electrolysis and efficiently replaceable to Pt. Why are they superior to other kinds of carbon electrodes? We noted

Table 3. Yield of Kolbe Dimers (R-R) for the Anodic Oxidation of Carboxylic Acids($R-CO_2H$)a) /%

Anode R-	Pt	GC-E	GC-A	Vitreous carbon	Baked carbon	Carbon
$CH_3O_2C(CH_2)_2-$	68	73	63	21b)	15b)	-
$CH_3O_2C(CH_2)_3-$	71	67	59	-	-	-
$CH_3O_2C(CH_2)_4-$	73	72	58	-	-	0
$CH_3(CH_2)_5-$	48	42	40	24—33b)	30b)	-
$CH_3O_2C(CH_2)_7-$	63	57	51	-	-	-
$PhOCH_2-$	40	44	36	23—25c)	-	-

a) CH_3OH/Py(4/1), Na(0.026 equiv.), 2 F/mol, 20 °C. b) R. Brettle et al., $(C_2H_5)_3N/CH_3OH$.13) c) R. Brettle et al., pyridine/C_2H_5OH.13) the correlation between the ratio(radical product/ionic products) in Table 1 and the apparent porosity of some carbons (Table 4). The ratio decreases with increasing of apparent porosity. Apparent porosity is supposed to indicate a quantity of pore and has a close relationship with adsorption ability.[14)] In the case of carbon, strong adsorptive properties of electrode make carboxylate ions remain for longer time near the surface of electrode, so that alkyl radicals R$^\bullet$ are liable to suffer further electro-oxidation. In the case of GC-E and GC-A, their adsorptive properties are much weaker than that of carbon, so that alkyl radicals R$^\bullet$ are liable to leave from electrode surface. Conclusively, some of glassy carbons are supposed to be promising anode materials for the Kolbe coupling, and it is considered that the surface character, especially adsorptive property is quite significant on the product composition in Kolbe reaction.

Table 4. Apparent Porosity and the Ratio (**5**/**1**+**2**+**3**) in Table 1 for Some Carbon Materials

	GC-E	GC-F	GC-G	Carbon
Apparent porosity /%	0.2 – 0.4	1 – 3	3 – 5	20 – 30
5/**1**+**2**+**3**	1.92	1.02	0.68	0

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9) All experiments of preparative electrolysis were performed according to the following general procedure. A carboxylic acid (16.7 mmol) and Na (0.01 g, 0.43 mmol) were dissolved in the mixed solvent of methanol(40 ml) and pyridine(15 ml) and electrolyzed at a constant current in an undivided cell. After the reaction, the mixture was then acidified with dil. HCl and extracted with ether. The combined ether was washed with water and dried over $MgSO_4$. The ether was removed and the residues were distilled. Distilled fractions were then analyzed by G.L.C.
10) Nippon Carbon Co., Ltd. EGM-62.
11) Gold sputtering on a carbon (Nippon Carbon Co., Ltd. EGM-62) was performed with JEOL Ion Sputter JFC-1100 ($\approx 10^{-3}$ Torr, DC, 1200 V, 15 mA, 20 min).
12) Diamond-like-Carbon coating on a graphite carbon was performed by Idemitsu Petrochemical Co., Ltd. The membrane thickness of coating was about 1.2 μm.
13) M. P. J. Brennan and R. Brettle, J. Chem. Soc., Perkin Trans. 1, **1973**, 257.
14) "Adsorption, Surface Area and Porosity," 2nd ed, ed by S. J. Gregg and K. S. W. Sing, Academic Press, New York(1982).

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