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SIMULTANEOUSLY OCCURRING HYDROXYLATION, HYDRATION, AND HYDROGENATION OF THE C=C BOND OF ALIPHATIC CARBOXYLIC ACIDS IN AQUEOUS SOLUTION BY GLOW DISCHARGE ELECTROLYSIS

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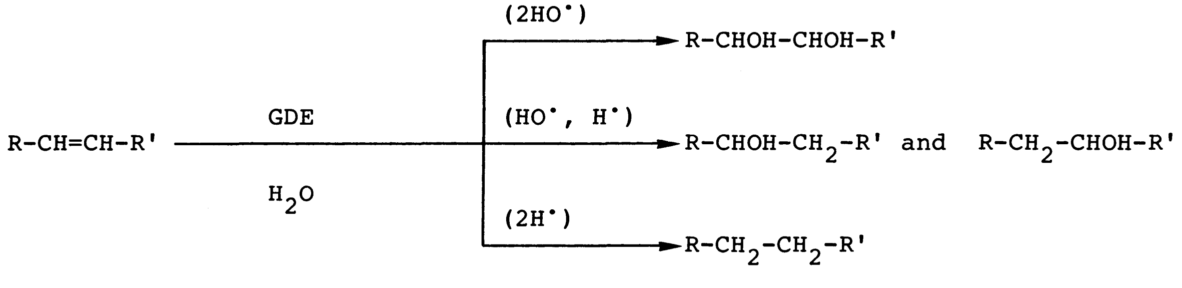
Glow discharge electrolyses of maleic and acrylic acids in carbonate-free distilled water simultaneously afford the products into which OH and/or H groups are introduced, indicating the addition reactions of OH and H radicals to the C=C bond.

Glow discharge electrolysis (GDE) is a type of chemical change due to the glow discharge between a substrate solution containing an electrolyte and an electrode in contact with the solution. Hickling1) has assumed that the GDE-promoted reaction is mainly initiated by OH and H radicals arising from the decomposition of water molecules with gaseous ions (H_2O^+) generated in the discharged zone. Recently, the present authors2) demonstrated that GDE of CD_3COOH in aqueous solution simultaneously gives rise to both $HOCD_2COOH$ and CD_2HCOOH. This could suggest the coupling of OH and H radicals with the CD_2COOH radical intermediate during the course of GDE. However, there is as yet no further information about the simultaneous participation of OH and H radicals in the GDE reaction of organic materials. In this communication, we wish to present a novel GDE reaction induced by both OH and H radicals, that is, their addition reactions with olefinic carboxylic acids which are strongly suggested by the simultaneous formations of the OH and/or H-introduced products as shown in the following scheme:



(R = R'= COOH or R = H and R'= COOH)

The substrate solution was prepared by dissolving maleic acid or acrylic acid into carbonate-free twice distilled water. The concentration was adjusted to 10 mM to avoid polymerization reaction. GDE was carried out for 80 mL of the solution using a single straight tube (S-cell) or a U-shaped tube (U-cell).[2) In the U-cell, the anode and cathode compartments were separated by a fine porosity glass frit and GDE was carried out in the anodic compartment. The anode was a platinum wire and the cathode was a coil of platinum wire. They were arranged so that the cathode was completely immersed in the solution and the anode was fixed so as to be in contact with the liquid surface. The reaction was done at 30±2 °C with saturation by argon and with constant stirring. The applied electric current was 40 - 90 mA at 750 V. The photooxidation with a H_2O_2/UV system, which is generally believed to be promoted by OH radicals,[3) was also carried out to compare with the results of GDE. The experiment was made for 10 mL of the substrate solution containing 0.01 mol H_2O_2 in a Pyrex glass vessel at 15±2 °C under argon atmosphere. A high-pressure 400W mercury lamp (Riko kagaku) was used as a light source.

The results of GDE are listed in Table 1, together with those of photooxidation. All the products listed were identified and determined by HPLC and isotachoic electrophoresis. A part of them (malic acid, tartaric acid, succinic acid, and propionic acid) were further identified by paper chromatography,[4) or GC-MS spectroscopy[5) after esterification with BuOH. The released carbon, corresponding to the amount of the products oxidized to gaseous compounds[6) (i.e., CO and CO_2), was determined by a total organic carbon analyzer.

Table 1 shows that GDE of both olefinic carboxylic acids gives rise to the products into which the OH and/or H groups are introduced: i.e., succinic acid, malic acid, and tartaric acid from maleic acid; and propionic acid, β-hydroxy propionic acid, lactic acid, and glyceric acid from acrylic acid. All of them, except succinic acid, were obtained only in the anode compartment when GDE was done with the U-typed cell. The cathodic formation of succinic acid from maleic acid was also observed in the electrolysis which was carried out as a control experiment. Thus, the electrochemical reduction may have an influence upon the formation of succinic acid during GDE. However, the electrolysis of acrylic acid did not lead to any chemical change other than the migration of the substrate from the cathode to the anode. This shows that the electrode reduction is negligible during the GDE reaction of acrylic acid.

As can also be seen from Table 1, the photooxidation gives only the hydroxylated products:

$$\text{R-CH=CH-R'} \xrightarrow[H_2O]{H_2O_2/UV} \text{R-CHOH-CHOH-R'} \qquad (\text{R = R'= COOH or R = H and R'= COOH})$$

Such a chemical reaction did not take place in the absence of H_2O_2, indicating that the photooxidation is promoted by OH radicals arising from the photolysis of

Table 1. Results of GDE and Photooxidation for Maleic and Acrylic Acids$^{a)}$

	GDE								Photooxidation$^{b)}$
	S-cell		U-cell				Control$^{c)}$		
Time/min	5	10	5		10		40		10
Current/mA	90	90	40		40		40		
Voltage/V	750	750	750		750		750		
			anode	cathode	anode	cathode	anode	cathode	
HOOCCH=CHCOOH$^{d)}$ /mM	6.20	4.05	8.20	10.0	6.37	8.02	12.9	6.95	3.40
$HOOCCH_2CH_2COOH$/mM	0.13	0.18	trace	0	0.09	trace	0	0.65	0
$HOOCCH(OH)CH_2COOH$/mM	0.28	0.47	0.16	0	0.29	0	0	0	0
HOOCCH(OH)CH(OH)COOH/mM	0.46	0.63	0.31	0	0.53	0	0	0	0.62
$(COOH)_2$/mM	1.19	2.25	0.51	0	0.98	0	0	0	1.54
HCOOH/mM	0.62	1.04	0.24	0	0.51	0	0	0	1.12
Released carbon$^{e)}$ /%	18.6	32.1	3.2$^{f)}$		18.3$^{f)}$		0$^{f)}$		10.67
CH_2=CHCOOH$^{d)}$ /mM	6.49	4.21	9.15	9.96	7.95	8.96	12.3	8.54	1.32
CH_3CH_2COOH/mM	0.19	0.38	0.09	0	0.20	0	0	0	0
$CH_2(OH)CH_2COOH$/mM	0.29	0.53	0.17	0	0.34	0	0	0	0
$CH_3CH(OH)COOH$/mM	0.25	0.47	0.12	0	0.25	0	0	0	0
$CH_2(OH)CH(OH)COOH$/mM	0.32	0.62	0.18	0	0.36	0	0	0	1.32
$HOCH_2COOH$/mM	0	0	0	0	0	0	0	0	1.10
OHCCOOH/mM	0	0	0	0	0	0	0	0	1.10
$(COOH)_2$/mM	0.42	0.72	trace	0	0.16	0	0	0	0.44
HCOOH/mM	0.58	0.96	0.04	0	0.21	0	0	0	0.63
Released carbon$^{e)}$ /%	15.4	27.8	1.7$^{f)}$		10.3$^{f)}$		0$^{f)}$		17.8

a) Initial substrate concentration 10 mM. b) Involves some products unidentified; one for maleic acid and two for acrylic acid. c) Denotes the electrolysis carried out with the U-cell. d) Denotes the substrate remaining in the system. e) Corresponds to the amount of the products oxidized to gaseous compounds (i.e., CO and CO_2). f) Determined for whole sample obtained from both anode and cathode compartments.

H_2O_2. Therefore, it is clear that both hydrated and hydrogenated products never result from the OH radical-induced reaction of the olefinic carboxylic acids in aqueous medium.

In conclusion, the present results reveals that water molecules break up in the course of GDE to generate both OH and H radicals, which then undergo the simultaneous addition to the C=C bond of the olefinic carboxylic acids, bringing about hydroxylation, hydration, and hydrogenation. The GDE technique, which enables water molecules to decompose to OH and H radicals, could be useful for studying radical reactions of various organic and also inorganic compounds in aqueous solution.

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References

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3) For example, N. A. Milas, P. F. Kurz, and W. P. Anslow, J. Am. Chem. Soc., 59, 543 (1937); R. Livingston and H. Zeldes, J. Chem. Phys., 44, 1245 (1966).

4) R_f values (0.24, 0.42, and 0.71) on a Whatman 3MM Chroma filter paper in the system AcOEt/AcOH/H_2O (50:12:10 v/v) were assigned to tartaric acid, malic acid, and succinic acid, respectively.

5) Propionic acid was identified by the MS data [m/z, 57(100), 29 (38), 75(13), 87(6)] of a peak in GLC of the BuOH-esterified reaction mixture.

6) CO and CO_2 were identified by GC analysis.

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