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Study on Electroreduction Mechanism of Aromatic Dicarboxylic Acids. Electrosynthesis of 1,4-Benzenedimethanol1)

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Synopsis. The electroreduction mechanisms of terephthalic acid and isophthalic acid in acidic solution were studied by molecular orbital (MO) calculations. Further, a practical stepwise route to 1,4-benzenedimethanol has been developed by the electroreduction of *p*-(hydroxymethyl)benzoic acid.

1,4-Benzenedimethanol (**4**) is of importance as a component of useful polymers,2) though a practical synthetic method has not yet been established. Namely, as a hitherto disclosed procedure for the synthesis of **4**, the chlorination of *p*-xylene followed by hydrolysis3) has been reported. However, the selectivity of the chlorination of each benzylic position is not necessarily satisfactory. The hydrogenation of terephthalic acid diester4) has also been reported, in which there still remains serious problems regarding the practical preparation of **4**, due to the vigorous reaction conditions and low yield of the product.

Incidentally, the electroreduction of aromatic carboxylic acids is both useful and a practical technique for the preparation of benzyl alcohols. We have therefore studied the synthesis of **4** starting from easily available terephthalic acid (**1**) by electrolysis. So far, it has been reported that the electroreduction of **1** in acidic aqueous media results in a nuclear reduction which affords 2,5-cyclohexadiene-1,4-dicarboxylic acid (**3**),5) while the electroreduction of **1** in aqueous ammoniacal media gives *p*-(hydroxymethyl) benzoic acid (**9**).6) However, no successful conversion of **1** to **4** has been mentioned in the literature.

In general, the mechanism of side chain reduction of aromatic carboxylic acid seems best accommodated7) by protonated carboxylic acid; the reduction is known to be promoted in a more acidic solution.8) Therefore, in order to investigate the possibility of a side-chain reduction of dicarboxylic acid **1** under the acidic conditions, we considered the reaction pathway of the electroreduction of **1**, compared with that of isophthalic acid (**5**), in terms of molecular orbital (MO) calculations; electroreduction of **5** in an aqueous acidic solution9) is reported to give 1,3-benzenedimethanol (**8**). According to our calculations, a direct reduction of **1** to **4** is unlikely to occur in acidic solution. We, therefore, investigated a combination of the electroreduction of **1** to **9** and that of **9** to **4** (two step conversion through **9**). In this paper, we discuss the mechanism and practical electroreduction of **9** for **4**.

Electroreduction Mechanism of 1 and 5 in Acidic Aqueous Media. Though no mechanistic study has so far been available concerning the exceptionally specific formation of nuclear reduced product **3** from **1** in an acidic media, it might be explained by assuming two different pathways (illustrated in Scheme 1): one involves a direct electroreduction of **1** followed by protonation (Route A), the other involves the protonation of **1** prior to electroreduction (Route B). A two-electron transfer should occur rather rapidly in an equilibrium state after the diprotonation of **1**, leading to the formation of **2**. The most important key step of each pathway (Route A and B) related to the product selectivity and rate determination may be the electron-uptake process of **1** and **2**, respectively. According to a MO calculation, the LUMO electron density of **1** is highly localized in the aromatic ring. Therefore, an electron uptake would take place, preferably, at the aromatic nuclear, affording **3** (Route A). On the other hand, an electron transfer on **2** would occur at the side chain to produce **4** (Route B), owing to the higher value of the LUMO electron density observed in the side chain of **2**.

Next, in order to assess the preferable route in Scheme 1, we compared the LUMO energy level of the key intermediate in the electron transfer. An intermediate having a lower LUMO energy would undergo an electron uptake, preferentially.10) The estimated value of the LUMO energy of **1** and **2** are shown in Scheme 1. The LUMO energy of **1** is lower than that of **2**, indicating that the electron uptake of **1** proceeds more smoothly than that of **2**. Thus, in turn, this fact suggests that Route A is preferable to Route B.

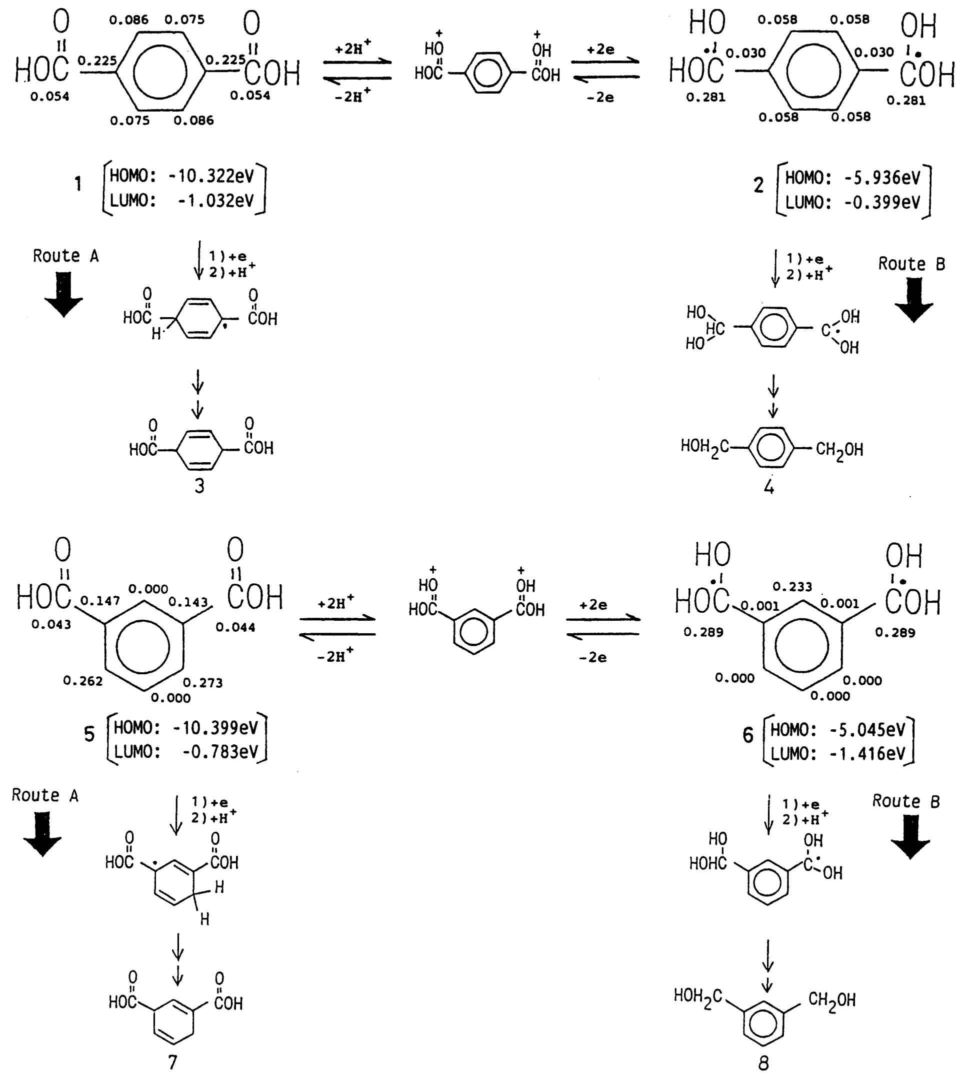
A MO calculation of meta derivative **5** was accomplished in a similar manner as that mentioned above, and opposite results were obtained. Thus, a reduction of **5** seems to occur, preferentially, according to Route B to give **8**, since the LUMO energy of **6** in Route B is lower than that of **5** in Route A.

Now, our calculations show a different reactivity of **1**, compared with that of **5**, suggesting the difficulty of a side-chain reduction of **1** in an acidic aqueous media;

Table 1. Electroreduction of Aromatic Carboxylic Acids[a)]

Entry	Substrate	Solvent electrolyte	Electricity passed F mol^{-1}	Product (Yield/%)[b)]
1	**9**	12% aq. NH_4OH	10	—
2	**9**	10% aq. Et_4NOTs	10	**4** (3)
3	**9**	10% aq. H_2SO_4	10	**4** (68)
4	**1**	10% aq. H_2SO_4	43	**3** (3)[c)]
5	**5**	10% aq. H_2SO_4	90	**8** (6)[c)]

a) The electroreduction was carried out under constant current of 5 A dm^{-2} with an H-shaped divided cell fitted with two lead electrodes at 40 °C. b) Isolated yield based on substrate. c) Detected as a single product.



Scheme 1. LUMO electron densities are shown, and the values in parentheses represent HOMO and LUMO energy level. Molecular structures were designed by using STERIC1[14] program; equations used for calculations are as follows, 1: 1*BENZ (.1.-COOH)(.4.-COOH)**, charge of the molecule=0, 2: 1*BENZ-(.1.-C(-OH)2.+.)(.4.-C(-OH)2.+.)**, charge of the molecule=0, 5: 1*BENZ-(.1.-COOH)(.3.-COOH)**, charge of the molecule=0, 6: 1*BENZ-(.1.-C(-OH)2.+.)(.3.-C(-OH)2.+.)**, charge of the molecule=0, and RHF-AM1[15] calculations have been curried out.

the higher reactivity of **1**, in comparison with that of **2**, would displace the equilibrium to Route A. We changed the synthetic strategy in order to study the electroreduction of monocarboxylic acid (**9**) in an aqueous acidic media, which is easily synthesized by the electrolysis of **1** in an aqueous ammoniacal media.

Electroreduction of Aromatic Carboxylic Acids. Electroreduction was carried out with two lead electrodes using an H-shaped two-compartment cell divided by an ion-exchange membrane. The results under various electrolysis conditions are summarized in Table 1.

In the electroreduction of **9**, a satisfactory current efficiency was attained in an aqueous acidic media (Entry 3), while under neutral conditions (Entry 2), the reduction was very slow and no appreciable amount of **4** could be detected under ammoniacal basic conditions (Entry 1).

Incidentally, the electroreduction of **1** under the same reaction conditions as Entry 3 gave a nuclear reduced product **3** without the detection of a side chain reduction (Entry 4), whereas that of **5** afforded a single product **8** (Entry 5).

Experimental

Melting points are uncorrected and were determined in open-ended capillaries. IR spectra were recorded on a Hitachi 285 grating spectrometer.

Calculations. The calculations were performed on a Fujitsu FACOM M360R using MOPAC.[11]

Apparatus. An H-shaped cell divided by an ion-exchange membrane (Asahi Glass Co., Ltd. Selemion CMV) was used; it was equipped with two lead plate electrodes (50 cm^2, 12 cm apart), stirring bars, and a thermometer. A vessel was immersed in a hot water bath at 40 °C and regulated dc power was supplied by Kikusui Electronics Co. Model PAD 35-60L.LP.

General Procedure. Electrochemical Reduction of *p*-(Hydroxymethyl)benzoic Acid (9). Into both the anode and cathode compartments was placed a 10% aqueous H_2SO_4 solution (200 g each). After regulated dc power (5 $A\,dm^{-2}$) was supplied at 40 °C, to the catholytes was portionwise added *p*-(hydroxymethyl)benzoic acid (**9**; 2.37 $g\,h^{-1}$, total 20.0 g, 0.131 mol) during the first 6 $F\,mol^{-1}$ (8.4 h). After electrolysis (10 $F\,mol^{-1}$, 14.0 h) at 40 °C, the catholyte was extracted with diethyl ether. The extract was washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (SiO_2, hexane/AcOEt, 3 : 1) to give **4** (13.0 g, 68.0%) as white crystal with an IR spectrums identical with that reported for the authentic material;[12] mp 113—116 °C (lit,[13] mp 118—119.4 °C).

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