CHEMISTRY LETTERS, pp. 1861-1864, 1994.

Simultaneous Epoxidation of 1-Hexene and Hydroxylation of Benzene during Electrolysis of Water

Kiyoshi OTSUKA,* Ichiro YAMANAKA, and Makoto HAGIWARA
Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

Epoxidation of 1-hexene and hydroxylation of benzene to phenol and hydroquinone occurred at the same time on the anode and the cathode, respectively, during electrolysis of water at room temperature. The most favorable anode and the cathode for these reactions were Pt black and the carbon whisker added with Pd black and Fe_2O_3, respectively.

The epoxidation of olefins is extremely important both in the current industrial process and organic synthesis because epoxide is one of the most useful synthetic intermediates. Except for the synthesis of ethylene oxide, all other commercial epoxidation reactions are indirect, multi-step co-oxidations. Moreover, these processes require a labile, explosive and expensive oxidant such as hydrogen peroxide, peracetic acid or ter-butyl hydroperoxide.[1-6]

The Cumene process and the analogous one for the synthesis of phenol and hydroquinone, both important synthetic intermediates in chemical industry, require multi-step operations for converting benzene to phenol and hydroquinone. Direct hydroxylation of benzene to these compounds remains a potentially attractive, stimulating a number of research works so far.[7-8]

Recently we have proposed a simple electrocatalytic method for the one-step synthesis of epoxycyclohexane and that of phenol under mild conditions. The new technique for the former used a nascent oxygen generated on the Pd anode during electrolysis of water.[9] However, the current efficiency for the synthesis of epoxide was quite low (≤4.5%). On the other hand, the synthesis of phenol was made possible by a reductively activated oxygen on the cathode during H_2-O_2 fuel cell reactions.[10] If the two methods are combined in a cell, we can expect epoxidation of olefins at the anode and hydroxylation of aromatics at the cathode. Thus, the purpose of this work is to demonstrate the simultaneous epoxidation of 1-hexene at the anode and hydroxylation of benzene at the

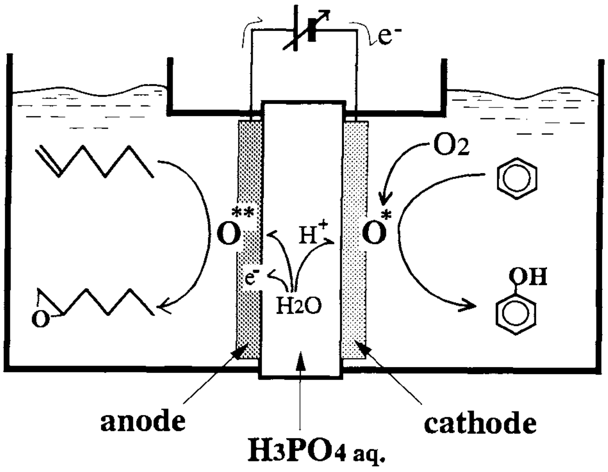

Fig. 1. Simultaneous epoxidation of 1-hexene and hydroxylation of benzene at the anode and the cathode compartments.

Table 1. Epoxidation of 1-hexene on various noble metal anodes

Anode	Amount of 1,2-epoxyhexane/ μmol	Charge passed / C	Current efficiency of epoxide /%
Pt black	74.5	50.5	28.5
Pd black	32.3	310.7	2.0
Rh black	1.2	233.1	0.1
Ru powder	2.1	32.3	1.3
Au powder	<0.1	3.6	0

cathode during electrolysis of water.

The reactor used and the principle of the method are shown schematically in Fig. 1. A silica-wool disk (21 mm diameter, 2 mm thickness) holding aqueous H_3PO_4 electrolyte (1 mol·dm^{-3}; 0.8 cm^3) separates the two compartments which contain pure benzene and 1-hexene (40 cm^3 each). The anode was prepared from various noble metal blacks (70 mg) mixed with Teflon powder (5 mg as a binder) by hot-press method. The cathode was prepared by the same method from a mixture of Pd black (20 mg), Fe_2O_3 (20 mg) and Teflon powder (5 mg). This cathode has been suggested as one of the best electrocatalysts for hydroxylation of benzene.11) Argon was bubbled into 1-hexene in the anode compartment and oxygen into benzene in the cathode compartment. The oxidations in both compartments were started by applying a voltage across the cell at 303 K.

Before we start the simultaneous oxidations at the cathode and the anode, the favorable electrocatalysts for the epoxidation of 1-hexene have been looked for. The cathode for these experiments was prepared from a mixture of Pt black (50 mg), graphite (20 mg) and Teflon powder (5 mg). The experiments were carried out in the absence of benzene in the cathode compartment at 303 K by applying a voltage of 1.7 V across the cell for 2 h. Argon was passed in both compartments. Table 1 shows the results of oxidation of 1-hexene for the anodes of different noble metal black or powder.

The results in Table 1 indicate that Pt black is the most active and selective anode for the synthesis of 1,2-epoxyhexane. The current efficiency for the formation of epoxide was remarkably high (29%) for the Pt black among the anodes tested in Table 1. The other products observed for the Pt black anode were 1-hexanal(29.3 μmol) > 2-hexanone(15.6) > 1-hexanoic acid(14.7) > pentanoic acid(7.7) and traces of several unidentified products. A trace of CO_2 was also observed.

The content of Teflon added to the Pt black anode affected the rate of epoxide formation remarkably. Decrease in the content of Teflon from 5 to 1 mg in 70 mg of Pt black increased the amount of 1,2-epoxyhexane formed in 2 h from 75 to 370 μmol . Thus, the experiments described below have been carried out using the Pt black anode (70 mg) added with 1 mg Teflon powder.

Figures 2 and 3 show the results of simultaneous oxidations of 1-hexene and benzene, respectively, as functions of applied voltage under the experimental conditions described above. The results of 1-hexene oxidation at the anode (Fig. 2) indicate that the reaction proceeds at an applied voltage of 0.5 V across the cell because oxygen is bubbled into benzene in the cathode compartment. 1,2-Epoxyhexane and 1-hexanal were the main products at lower applied voltage (<1.5 V), but the formation of 1,2-epoxyhexane was enhanced significantly at 1.7 V, giving the maximum current efficiency of epoxide at this applied voltage.

The results in Fig. 3 show that the hydroxylation of benzene at the cathode occurs at an applied voltage >0.5 V. The rates of phenol and hydroquinone formations show maxima at the applied voltage of 1.2—1.7 V.

The results in Figs. 2 and 3 suggest that the optimum applied voltage for simultaneous syntheses of 1,2-epoxyhexane and phenol is 1.7 V under the experimental conditions in this work. Under this applied voltage, we have observed that both products accumulate linearly with reaction time in the anode and cathode compartments.

The epoxidation at the anode may be ascribed to a nascent oxygen generated due to the electrolysis of water in the aqueous solution of H_3PO_4 in the membrane.[9] The possibility of a wide range of reactive oxygen or hydrogen oxide species being created on the anode cannot be excluded. Although the system is quite complex both chemically and physically, the specific catalysis of Pt black for the synthesis of epoxide is definitely to be clarified in detail. On the other hand, we have already suggested that the hydroxylation of benzene at the cathode can be ascribed to OH radicals generated during the reduction of oxygen in the cathode compartment.[10,11]

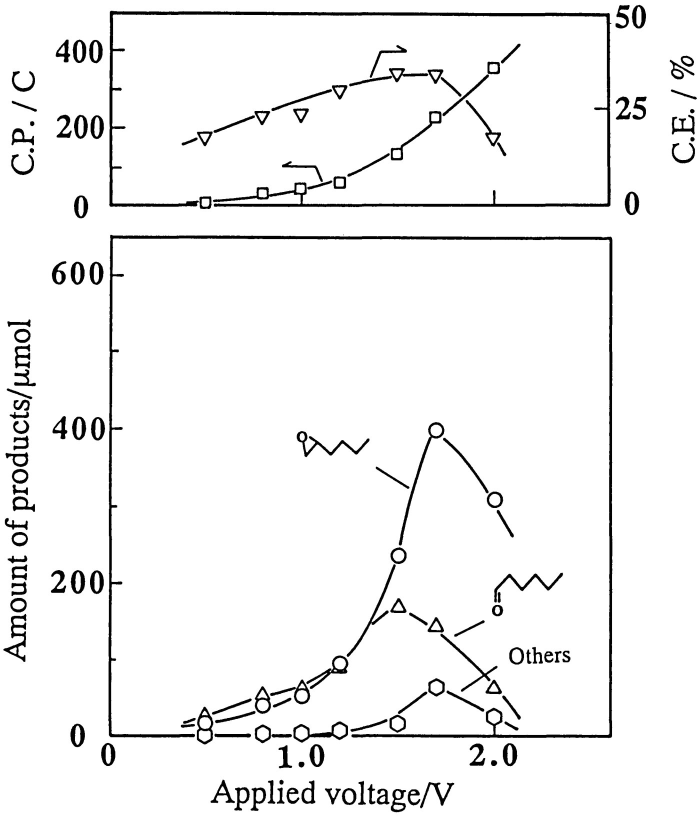

Fig. 2. Epoxidation of 1-hexene at the anode as functions of applied voltage. (C.P.), charge passed in 2 h ; (C.E.), current efficiency of epoxide formation.

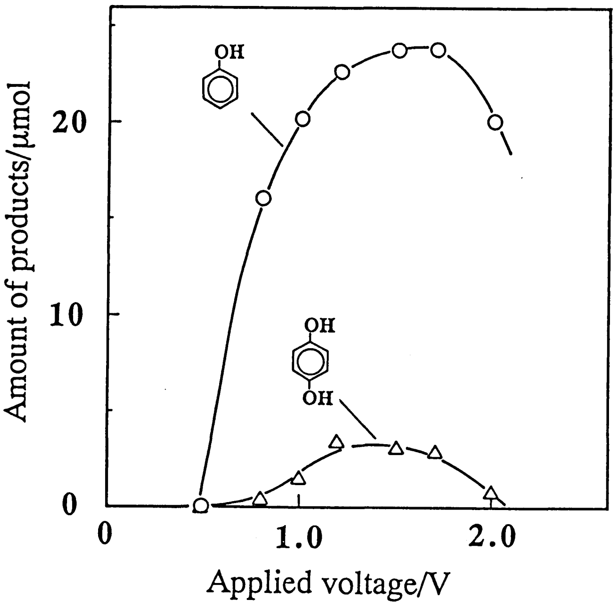

Fig. 3. Hydroxylation of benzene at the cathode as functions of applied voltage.

In conclusion, the electrolysis using the cell composed of a H_3PO_4 membrane, the Pt black anode and the carbon whisker cathode with Pd black and Fe_2O_3 produced 1,2-epoxyhexane from 1-hexene at the anode and phenol and hydroquinone from benzene at the cathode at the same time.

References

1) R. Landau, G. A. Sullivan, and D. Brown, *CHEMTECH*, **1979**, 106.
2) R. A. Sheldon and J. K. Kochi, "Metal Catalyzed oxidations of Organic Compounds," Academic Press, New York (1981).
3) H. Mimoun, *Catal. Today*, **1**, 281 (1987).
4) R. A. Sheldon, *Stud. Surf. Sci. Catal.*, **66**, 573 (1991).
5) B. Notari, *Stud. Surf. Sci. Catal.*, **67**, 243 (1991).
6) G. Goor, "Catalytic Oxidations with Hydrogen Peroxide as Oxidant," Kluwer Academic Pub., ed by G. Strukul, Dordrecht (1992), p. 13.
7) S. Ito and K. Sasaki, *Yuki Gosei Kagaku Kyokaishi*, **41**, 839 (1983); A. Kunai and K. Sasaki, *Kagaku to Kogyo,* **42**, 459 (1989), and references therein.
8) "Metalloporphyrins Catalyzed Oxidations," ed by F. Montanari and L. Casella, Kluwer Academic Pub., Dordrecht (1994).
9) K. Otsuka, M. Yoshinaka, and I. Yamanaka, *J. Chem. Soc., Chem. Commun.*, **1993**, 611.
10) K. Otsuka, I. Yamanaka, and K. Hosokawa, *Nature* (London), **345**, 697 (1990); K. Otsuka, M. Kunieda, and H. Yamagata, *J. Electrochem. Soc.*, **139**, 2381 (1992); I. Yamanaka and K. Otsuka, *J. Chem. Soc.*, *Faraday Trans*., **89**, 1791 (1993).
11) K. Otsuka, M. Kunieda, and I. Yamanaka, in "New Developments in Selective Oxidation," ed by V. Cortés Corberán and S. Vic Bellón, Elsevier, Amsterdam (1994), p. 703.

(Received May 23, 1994)