Epoxidation of Cyclohexene with the Nascent Oxygen generated by Electrolysis of Water

Kiyoshi Otsuka,* Masahiro Yoshinaka and Ichiro Yamanaka

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

The active oxygen generated on the palladium anode during electrolysis of water epoxidized cyclohexene selectively at room temperature.

In present chemical industrial processes, epoxidation of alkenes requires an oxidant such as hydrogen peroxide, peracetic acid or *tert*-butyl hydroperoxide.[1–6] However, these oxidants are labile, explosive and expensive. Therefore, a new process using dioxygen as oxidant or a novel technique using mild conditions is desirable. In this report, we propose an easier, safe and inexpensive method for the epoxidation of alkenes. The new technique uses the nascent oxygen generated by means of electrolysis of water. We have chosen the epoxidation of cyclohexene as an example.

The reactor used and the principle of the method are represented schematically in Fig. 1. The proton conducting membrane at the centre of the two compartments is a silica-wool disk (21 mm diameter, 2 mm thickness) containing aqueous H_3PO_4 (1 mol dm^{-3}; 0.8 cm^3). The anode was prepared from precious metal blacks (70 mg) mixed with

Teflon powder (5 mg) by the hot-press method. The cathode was prepared by the same method from a mixture of Pt black (20 mg), graphite (50 mg) and Teflon powder (5 mg). Argon was bubbled into cyclohexene (40 ml) in the anode compartment to remove the oxygen evolved during the electrolysis. Argon (97 kPa) and water vapour (4 kPa) were passed into the cathode compartment. The oxidation of cyclohexene was started by applying a voltage between the anode and cathode at 303 K. Water vapour dissolved in the membrane was electrolysed during the reaction.

Table 1 shows the amount of cyclohexene oxide (denoted as epoxide hereafter), the selectivity to epoxide, the current efficiency for epoxide formation (CE) and the charge passed observed for the anodes of the mixture of precious metal blacks and graphite. The experiments were carried out by applying a constant voltage of 1.7 V for 3 h. The current efficiency for epoxide formation was calculated assuming 2 F are required to give 1 mol of epoxide. The epoxide selectivity in Table 1 means the fraction of epoxide in the sum of the oxygenated products. The other products observed were cyclohexene-1,2-diol, cyclohexanone, cyclohexanol, cyclohex-2-en-1-one and cyclohex-2-en-1-ol. The relative quantites of these products were quite different for the different
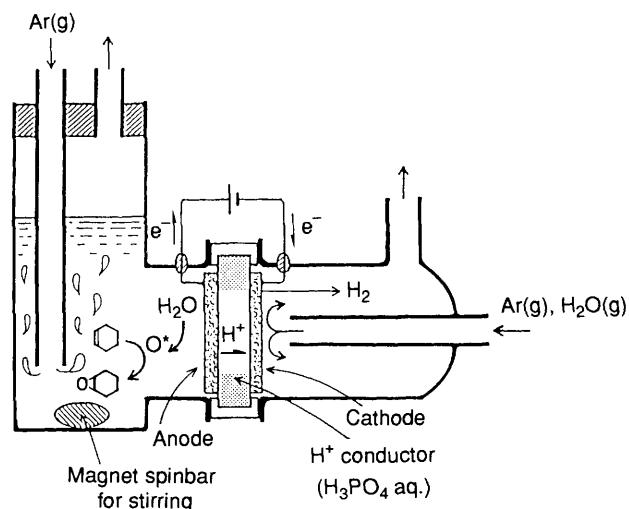

Ar(g)

Magnet spinbar for stirring

H^+ conductor
$(H_3PO_4 aq.)$

Fig. 1 Schematic diagram of the reactor for epoxidation of cyclohexene during water electrolysis

Table 1 Epoxidation of cyclohexene with various anodes during electrolysis of water

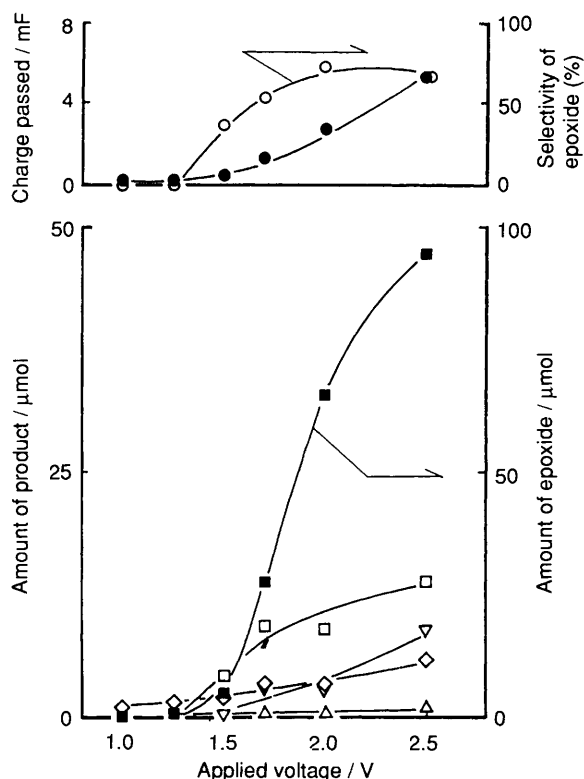| Anode | Charge passed/mF | Cyclohexene oxide | | CE (%) |
		Yield/ 10^{-6} mol	Selectivity (%)	
Pd black	4.41	98.5	47.6	4.5
Pt black	2.95	17.0	12.6	1.2
Rh black	4.76	2.4	3.2	0.1
Ru black	7.56	70.7	20.7	1.9
Au black	0.22	1.1	9.2	1.0
Graphite	0.58	1.1	1.2	0.4

Fig. 2 Oxidation of cyclohexene as a function of applied voltage. (■) epoxide; (∇) cyclohexene-1,2-diol; (◇) cyclohexanone; (△) cyclohexanol; (□) cyclohex-2-en-1-one and cyclohex-2-en-1-ol; (○) selectivity to epoxide; (●) charge passed.

anodes tested. The results in Table 1 show that the Pd black anode is the most active and selective for the formation of epoxide. Therefore, further studies have been carried out for this anode as described below.

Fig. 2 shows the effect of the applied voltage between the anode and the cathode on the amounts of each product, the charge passed, and on the selectivity of epoxide. The experiments were carried out at constant voltages for 45 min at 303 K. The oxygenates of cyclohexene were not produced at <1.25 V (except for cyclohexanone). The current and the formation of epoxide was accelerated at >1.5 V. The selectivity of epoxide increased to 75% at >2.0 V. The evolution of hydrogen and oxygen was observed in the cathode and anode compartments, respectively, at 1.5 V.

These observations strongly suggest that the epoxidation of cyclohexene results from the electrolysis of water.

The bubbling of oxygen instead of argon into the cyclohexene in the anode compartment did not cause any oxidation of cyclohexene under open circuit conditions at 303 K. Moreover, under an applied voltage of 1.70 V, the replacement of argon by oxygen did not influence the results of cyclohexene oxidation (except for cyclohexanone formation) within experimental error. These observations show that the oxygen evolved in the anode compartment during the electrolysis of water does not affect the epoxidation of cyclohexene. Therefore, the nascent oxygen, probably oxygen atoms, generated on the Pd-cathode by water electrolysis must be responsible for the epoxidation.

Reaction temperature affected the rate of epoxidation as well as the distribution of products remarkably. The rate of epoxide formation was maximum at 280–300 K and decreased sharply at >300 K. No epoxide was produced at ≥343 K. The rates of formation of cyclohexene-1,2-diol, cyclohex-2-en-1-ol and cyclohex-2-ene-1-one also decreased at >300 K. In contrast to these products, cyclohexanone formation increased drastically at temperatures above 300 K. The selectivity to the epoxide was improved with a decrease in reaction tempertature, to 80% at 260 K.

Although the reaction mechanism for the formation of each product cannot be clarified on the basis of the present results, the quite different kinetic behaviour observed for cyclohexanone and the other products implies that the reaction mechanism for cyclohexanone differs from that of the other products. Cyclohexanone is probably formed by a Wacker-type reaction mechanism via the redox of $Pd^0 \leftrightarrow Pd^{II}$. All other products, however, may be formed via the reaction of cyclohexene with the active oxygen generated on Pd^0.

In conclusion, the electrolysis of water by using Pd black as the anode enabled the epoxidation of cyclohexene at room temperature cogenerating hydrogen at the cathode.

References

1 R. A. Sheldon and J. A. van Doorn, J. Catal., 1973, 31, 427, 438.
2 R. A. Sheldon, J. Mol. Catal., 1980, 7, 107.
3 R. Landau, G. A. Sullivan and D. Brown, CHEMTECH., 1979, 602.
4 M. Mimoun, I. Seree do Roch and L. L. Sajus, Tetrahedron, 1970, 26, 37.
5 G. Goor, G. Prescher and M. Schmidt, Stud. Surf. Sci. Catal., 1990, 55, 71.
6 B. Notari, Stud. Surf. Sci. Catal., 1991, 67, 243.