Stabilization of Hydroperoxides by Means of the Formation of Inclusion Compounds with β-Cyclodextrin

Yoshihisa MATSUI, Haruki NARUSE, Kazuo MOCHIDA and Yoshio DATE

Department of Agricultural Chemistry, Shimane University, Nishikawazu-cho, Matsue

(Received March 16, 1970)

Cyclodextrins are known to stabilize a number of labile materials by means of inclusion.[1-3] We wish to report that hydroperoxides are also stabilized by the formation of inclusion compounds with β-cyclodextrin (I).

It is known[4] that *t*-butyl hydroperoxide (II) decomposes moderately at 95—100°C and explosively at 109°C. However, the crystalline adduct[5] (III) of I with II showed no change under these conditions. When the rate of the pyrolysis of II in III was measured at 160°C by means of the iodometric method, a moderate decrease of the hydroperoxide content was observed (Fig. 1). The crystalline adduct (IV) of I with *t*-amyl hydroperoxide decomposed more slowly than III at 160°C. Similarly, it was found that hydroperoxides such as *n*-butyl, isoamyl, *s*-octyl, and cumene hydroperoxides are stabilized by the formation of inclusion compound with I.

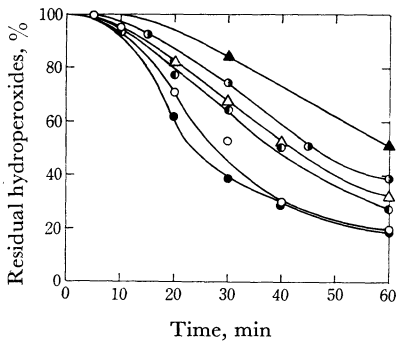

Fig. 1. Effect of I on the rate of the pyrolysis of hydroperoxides at 160°C.
△ III, ▲ IV, ○ II (0.11M) in H_2O,
◐ II (0.11M) + I (0.01M) in H_2O,
◑ II (0.11M) + I (0.02M) in H_2O,
● II (0.11M) + D-glucose (0.07M) in H_2O

The depression of pyrolysis of hydroperoxides by the interaction with I was also observed in an aqueous solution. As shown in Fig. 1, the rate of the pyrolysis of II (0.11M) in an aqueous solution was markedly decreased by the addition of 0.01M of I. The higher the concentration of I, the slower is the rate. However, the addition of D-glucose (0.07M) had no effect on the pyrolysis rate. These results clearly indicate that I stabilizes II by means of inclusion.

The stabilizing effect may be due to the formation of the strong hydrogen bonding between I and II.[5] The fact that the pyrolysis of II in an aqueous solution was depressed by the addition of I indicates that the hydrogen bond between I and II is stronger than that between I and water. It is also possible that the prevention of a chain mechanism in pyrolysis of hydroperoxides by means of inclusion may cause the stabilizing effect.[3]

1) F. Cramer, *Chem. Ber.*, **84**, 851 (1951).
2) H. Schlenk, D. M. Sand and J. A. Tillotson, *J. Amer. Chem. Soc.*, **77**, 3587 (1955).
3) J. L. Lach and T.-F. Chin, *J. Pharm. Sci.*, **53**, 924 (1964).
4) N. A. Milas and D. M. Surgenor, *J. Amer. Chem. Soc.*, **68**, 206 (1946).
5) Y. Matsui, H. Naruse, K. Mochida and Y. Date, This Bulletin, **43**, 1909 (1970).