Promotion of Charge-transfer Complex Formation by γ-Cyclodextrin

By NAGAO KOBAYASHI,* AKIHIKO UENO, and TETSUO OSA*
(*Pharmaceutical Institute, Tohoku University, Aobayama, Sendai* 980, *Japan*)

Summary The formation of a charge-transfer complex between sodium α-naphthylacetate and picric acid was promoted markedly by γ-cyclodextrin but not significantly by β-cyclodextrin.

CYCLODEXTRINS, which are torus-shaped oligosaccharides, form inclusion complexes with various substrates.[1] Recent studies have shown in particular that γ-cyclodextrin (γ-CD) can include two aromatic molecules per CD molecule because of the large size of its cavity.[2-4] In view of this characteristic of γ-CD, we have attempted to discover if the addition of γ-CD to a system in which charge-transfer (CT) complex formation is usually not observed promotes CT complex formation. Intensification of the CT band would be expected if γ-CD could include both electron donor and acceptor molecules in its cavity simultaneously.

We chose sodium α-naphthylacetate (α-NA) and picric acid (PA) as electron donor and acceptor molecules, respectively, with borate buffer (pH 9·18, 25 °C) as solvent, and concentrations of 10^{-2} mol l^{-1} for all reagents. The absorption spectra of solutions containing only PA (system I), PA and α-NA (II), or PA and γ-CD (III) exhibited only one distinct peak with an absorption coefficient (ε) of 14,700 at 350—360 nm. However, the addition of γ-CD to (II) or α-NA to (III) (system IV) led to a change in the colour of the solution from yellow to red and the appearance of a new peak (ε 2200) at 510 nm. Together with this change in the absorption spectrum, a change in the c.d. spectra was also observed. Although system (III) displayed a peak with [θ] 270 at 360 nm and a trough with [θ] 100 at 388 nm, which suggests a certain amount of interaction between PA and γ-CD, perhaps by inclusion of PA, the addition of α-NA resulted in a decrease in the absolute intensities of the peak and the trough and a new peak with [θ] 95 at 510 nm. We can rationalise these observations by assuming that CT complex formation does occur between α-NA and PA in γ-CD. Namely, the decrease in the absolute intensities of the peak at 360 nm and the trough at 388 nm may be explained in terms of competition between PA and α-NA for complex formation with γ-CD. System (IV) showed all the absorption and c.d. peaks, and we conclude that the 510 nm band is produced by the CT complex in the hydrophobic cavity of γ-CD.

The effect of β-CD on the formation of a CT complex between PA and α-NA was also studied similarly. The addition of β-CD to system (II) caused a change in colour from yellow to pale orange. Although we observed a slight increase in the intensity of the absorption in the 460—560 nm region of the visible spectrum, no significant c.d. peak was detected in this region.

Thus we have shown that γ-CD can promote CT complex formation by including both electron donor and acceptor in the same cavity.

(*Received*, 21*st January* 1981; *Com.* 071.)

[1] M. L. Bender and M. Komiyama, 'Cyclodextrin Chemistry,' Springer-Verlag, Berlin, 1978.
[2] A. Ueno, K. Takahashi, and T. Osa, *J. Chem. Soc., Chem. Commun.*, 1980, 921.
[3] A. Ueno, K. Takahashi, Y. Hino, and T. Osa, *J. Chem. Soc., Chem. Commun.*, 1981, 194.
[4] I. Tabushi, R. En, and Y. Kuroda, 41st Annual meeting of the Chemical Society of Japan, Osaka, 1980, Abstract II, p. 876.