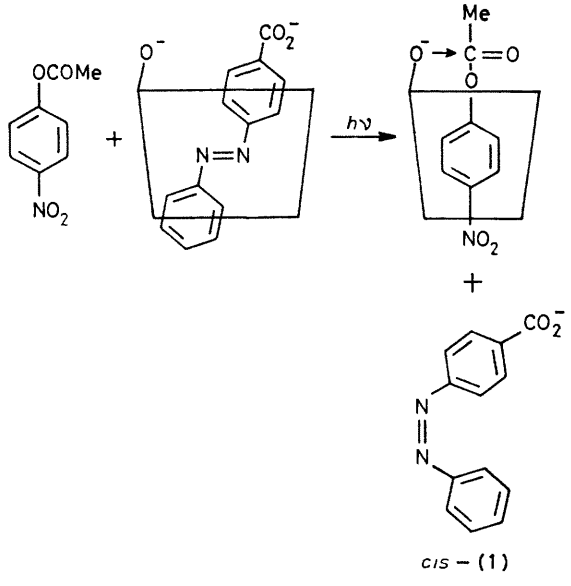
Photoregulation of Catalytic Activity of β-Cyclodextrin by an Azo Inhibitor

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

Summary The hydrolysis of *p*-nitrophenyl acetate catalyzed by β-cyclodextrin can be photoregulated by means of *trans–cis* photoisomerization of potassium *p*-(phenylazo)benzoate.

ORGANISMS on earth have developed various photosensitive systems in which light acts as a trigger, *via* complex pathways to cause direct responses or physiological changes. Indeed, photosensitive systems are ubiquitous in nature, but in no case is the mechanism by which the light energy is converted into the final responses known at molecular level. As one approach to elucidate the role of light in biological processes, some experiments have been carried out by enzymes with a photoresponsive group incorporated near the active site or systems composed of both enzymes and photoresponsive inhibitors, and the photoregulation of enzyme activity at the molecular level has been discussed.[1–3] A new method of investigation of the photocontrol of molecular functions by artificial systems has recently been made available by the photocontrolled complex formation performed with photochromic cyclodextrin.[4] We report here photocontrol of catalytic activity by a very simple system; the catalytic activity of β-cyclodextrin (β-CD) in ester hydrolysis can be photoregulated in the presence of potassium *p*-(phenylazo)benzoate (**1**).



cis – (**1**)

Photoirradiation of (**1**) was carried out with a 500 W Xenon lamp using a Corning 7-37 filter which passed light of 320—390 nm. The percentage of photostationary *cis*-isomer was estimated from the absorbance at 322 nm to be in the range of 55—65%. The hydrolysis of *p*-nitrophenyl acetate ($2{\cdot}5 \times 10^{-5}$ mol l^{-1}) at 25 °C was followed by measuring the absorbance at 390 nm (pH 8·7, Tris buffer). The reaction was initiated by addition of a stock solution of the ester in acetonitrile to the solutions of β-CD ($2{\cdot}5 \times 10^{-4}$ mol l^{-1}) and (**1**) ($0{\cdot}00$—$1{\cdot}67 \times 10^{-3}$ mol l^{-1}) before and after photoirradiation. Good pseudo-first-order rate data were obtained.

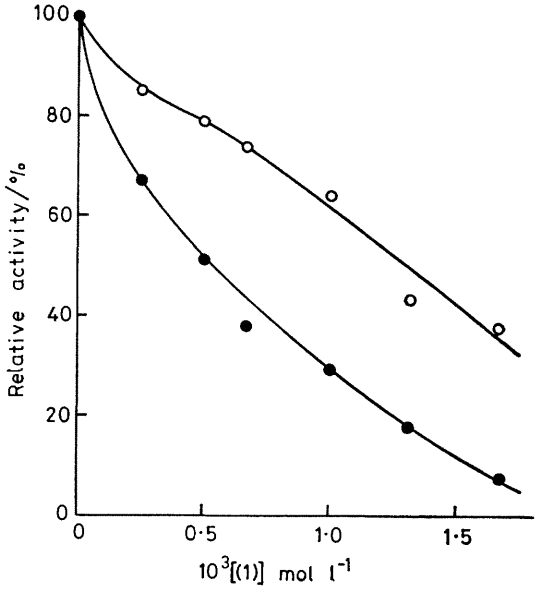


FIGURE. Effect of light in the hydrolysis of *p*-nitrophenyl acetate ($2{\cdot}5 \times 10^{-5}$ mol l^{-1}) catalysed by β-CD ($2{\cdot}5 \times 10^{-4}$ mol l^{-1}) at varying concentrations of (**1**) (25 °C, pH 8·7, Tris buffer); ●: before photoirradiation, ○, after photoirradiation; relative activity/% = $100(k_{obs} - k_{un})/k_{\beta\text{-CD}} - k_{un})$ where k_{obs} and k_{un} denote the rate constants when both and neither of β-CD and (**1**) are present, and $k_{\beta\text{-CD}}$ is the rate constant in the presence of only β-CD ($k_{un} = 1{\cdot}17 \times 10^{-4}$ s^{-1}, $k_{\beta\text{-CD}} = 1{\cdot}56 \times 10^{-4}$ s^{-1}).

The effect of light on the catalytic activity of β-CD at varying inhibitor concentrations is shown in the Figure where catalytic activity is normalized to that of β-CD after correcting for the buffer-catalysed rate. The data show the ability of light to convert the *trans*-isomer into the *cis*-isomer of (**1**) and the concurrent decrease in inhibiting the catalytic action of β-CD may be explained by the mechanism shown in the Scheme, where *trans*-(**1**) binds to β-CD more strongly than *cis*-(**1**). Since neither isomer of (**1**) exhibits catalytic activity, this reaction is solely responsible for the photocontrol of the hydrolysis. Examination of molecular models suggests that the geometry of *cis*-(**1**) disfavours a stable complex with β-CD, this host–guest

structural relationship being consistent with the above result. This system is reversible since the *cis* form of (**1**) reverts spontaneously to the original *trans* form, permitting an 'on–off' control of the catalytic activity.

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