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STEREOSELECTIVE RATE ENHANCEMENT OF MICELLE-CATALYZED HYDROLYSIS OF o-NITROPHENYL-β-D-GLUCOPYRANOSIDE

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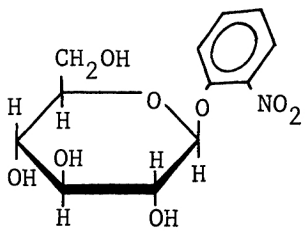
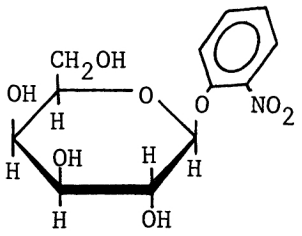
The rate of hydrolysis of o-nitrophenyl-β-D-glucopyranoside was largely enhanced in the presence of cationic micelle and phenylboronic acid under alkaline conditions, while that of o-nitrophenyl-β-D-galactopyranoside was much less enhanced.

A number of studies have been undertaken about the enzyme-mimic hydrolysis by using catalysts such as functional polymers,[1,2] peptides,[3-5] cyclodextrins,[6,7] micelles[8-13] or other hydrophobic aggregates[14,15] etc. With respect to acetal hydrolysis or glycoside hydrolysis which is important in biochemistry, detailed study was undertaken about the acid-catalyzed hydrolysis of the model compounds such as 2-(substituted phenoxy)tetrahydropyrans in the presence of anionic surfactants.[16] On the other hand, it is generally known that phenylboronic acid has a tendency to form esters with sugars such as glucose under alkaline conditions.[17] The resultant esters will be more hydrophobic and thus will be incorporated into micelle. The author has noted therefore the alkali-catalyzed hydrolysis of glucopyranoside and galactopyranoside in the presence of both phenylboronic acid and cationic micelle, about which very few studies have been undertaken thus far.

In the present paper, the author likes to describe the first successful study in accelerating the base-hydrolysis of o-nitrophenyl-β-D-glucopyranoside (o-NPGL) fairly selectively as compared with o-nitrophenyl-β-D-galactopyranoside (o-NPGA) which has the configuration very similar to o-NPGL.



o-NPGL



o-NPGA

The rates of the reaction were followed by observing the absorption of the o-nitrophenolate anion spectrophotometrically at 420 nm in 0.05 mol dm^{-3} phosphate buffer at pH 11.4 at 25°C. The kinetic data are summarized in Table 1.

Table 1. Pseudo-first-order rate constant ($k_{obsd}x10^5$ min^{-1})[a)]

Conditions	k_{obsd}	
	o-NPGL	o-NPGA
None	1.4	3.7
HTAC	3.5	9.6
Phenylboronic acid[b)]	1.6	3.5
HTAC-Phenylboronic acid[b)]	22.2	9.1
HTAC-Boronic acid[b)]	3.1	9.3
TEAC	1.4	3.3
TEAC-Phenylboronic acid[b)]	1.4	3.5
SDS	1.5	3.3
SDS-Phenylboronic acid[b)]	1.4	3.7

a) Observed at pH 11.4 (0.05 mol dm^{-3} phosphate buffer), [o-NPGL] = [o-NPGA] = $5x10^{-3}$ mol dm^{-3}, [HTAC] = $1x10^{-2}$ mol dm^{-3}, [phenylboronic acid] = $4x10^{-3}$ mol dm^{-3}, [boronic acid] = $4x10^{-3}$ mol dm^{-3}, [TEAC] = $1x10^{-2}$ mol dm^{-3}, [SDS] = $5x10^{-3}$ mol dm^{-3} at 25°C.

b) The concentrated solutions of phenylboronic acid and boronic acid were adjusted to pH 11.4 by NaOH before adding to the reaction systems.

It should be noted that in the presence of both $4x10^{-3}$ mol dm^{-3} phenylboronic acid and $1x10^{-2}$ mol dm^{-3} hexadecyltrimethylammonium chloride (HTAC) the hydrolytic rate of o-NPGL is extremely increased (ca.16 times) while that of o-NPGA is much less increased (ca.2.5 times). On the other hand, in the presence of only HTAC the hydrolytic rates of both o-NPGL and o-NPGA are increased only by 2.5-2.6 times. Phenylboronic acid alone does not bring about rate enhancement, too. Furthermore, the anionic surfactant, sodium dodecylbenzenesulfonate (SDS), or the low molecular weight ammonium salt, tetraethylammonium chloride (TEAC), does not cause rate enhancement. Addition of both HTAC and boronic acid instead of phenylboronic acid also does not give large rate enhancement, which suggests that the hydrophobicity of phenylboronic acid plays an important role for the acceleration of o-NPGL hydrolysis.

The small rate enhancement of the hydrolysis of both o-NPGL and o-NPGA in the presence of only HTAC seems to be due to the enrichment of hydroxide ion in the HTAC cationic micelle. The large rate enhancement of the hydrolysis of o-NPGL by the combination of HTAC and phenylboronic acid is probably ascribed to the large solubilization of o-NPGL complexed with phenylboronic acid into the HTAC micelle, whereas such rate enhancement is not seen for o-NPGA. Failure to accelerate the hydrolysis of o-NPGA may be due to the difference in the complexation modes with phenylboronic acid, although certain other reasons are unknown at present.

In Fig.1 are shown the pseudo-first-order rate constants (k_{obsd}) as a

function of the concentration of phenylboronic acid (C_p). It should be noted that k_{obsd} for o-NPGL increases remarkably in the presence of HTAC as C_p increases. In fact, the hydrolytic rate of o-NPGL is enhanced by ca.25 times when both HTAC ($1x10^{-2}$ mol dm^{-3}) and phenylboronic acid ($8x10^{-3}$ mol dm^{-3}) are present, as compared with that in the absence of HTAC. In the absence of HTAC, k_{obsd} for o-NPGL remains constant even when phenylboronic acid is added. On the other hand, k_{obsd} for o-NPGA is virtually constant even when both HTAC and phenylboronic acid are present, which is in striking contrast with that for o-NPGL. In the absence of HTAC, k_{obsd} for o-NPGA is also unaltered on addition of phenylboronic acid.

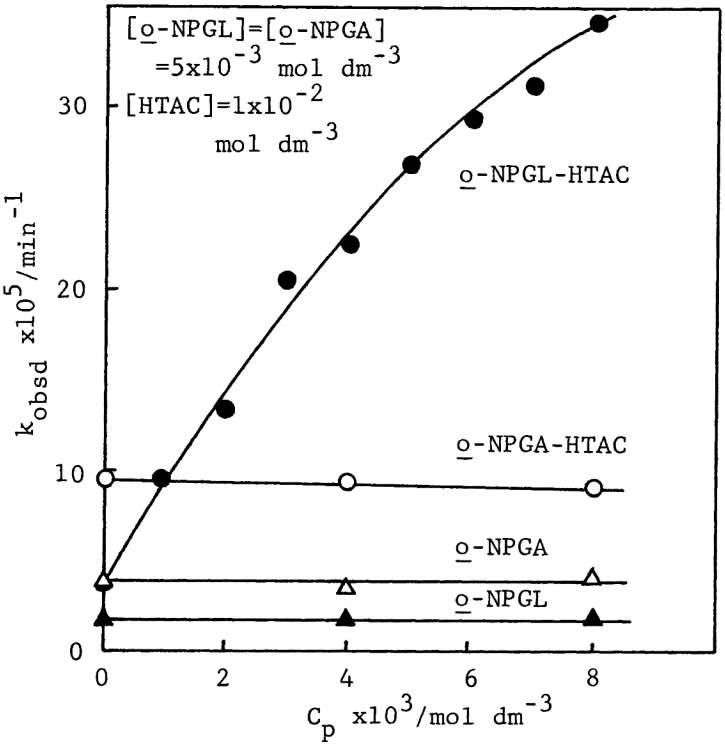


Fig.1. Plots of pseudo-first-order rate constants (k_{obsd}) as a function of phenylboronic acid concentration (C_p); pH 11.4 at 25°C.

In the present study, the selective acceleration of the hydrolysis of o-NPGL has been accomplished for the first time, although the reasons for the selectivity are uncertain. Study along this line is now in progress.

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