# Efficient Catalytic Hydrolysis of Disaccharides by Cerium(IV) Ion at pH 7

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$Ce^{IV}(NH_4)_2(NO_3)_6$ effectively catalyses hydrolysis of various disaccharides such as sucrose, maltose, lactose, and cellobiose at pH 7.0, and activation energy for sucrose hydrolysis was found to be 14.4 kcal $mol^{-1}$, which is remarkably smaller than that by 0.18 N HCl, 30 kcal $mol^{-1}$.

Artificial hydrolytic catalysts for saccharides are fundamentally important for chemical manipulation of sugars and saccharides. Recently, catalytic or stoichiometric activities of lanthanoide ions for hydrolysis of DNA, RNA and the related compounds[1] and also peptides[2] have been actively investigated, however there is no report regarding catalytic activity of lanthanoide ions for saccharides hydrolysis. In the course of our studies to investigate chemical conversion of saccharides into useful chemicals,[3] we found that $Ce^{IV}(NH_4)_2(NO_3)_6$ efficiently catalyses hydrolysis of disaccharides such as sucrose, maltose, lactose, and cellobiose (Figure 1) under neutral conditions. Here we report the catalytic activities of the cerium(IV) ion for hydrolysis of disaccharides, especially sucrose.

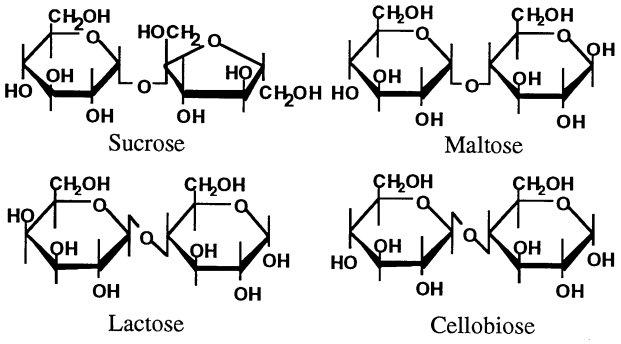


**Figure 1.** Disaccharides.

Hydrolyses of disaccharides (0.10 mol $dm^{-3}$) were carried out in the presence of $Ce^{IV}(NH_4)_2(NO_3)_6$ (5.0 x $10^{-3}$ mol $dm^{-3}$) at pH 7.0 (Tris buffer, 0.05 mol $dm^{-3}$) and 40 - 100 ℃. The catalytic activities were estimated by pursuing decrease of the disaccharides concentrations or increase of the products with HPLC (Waters, LC Module 1 plus, equipped with differential refractometer, Waters 410; Sugar-Pak Ca column). The reaction products were D-glucose and D-fructose for sucrose, and D-glucose for maltose, lactose, and cellobiose. Since other products were not detected and furthermore the decreasing concentrations of substrates were completely consistent with the increasing concentrations of products, reactions other than hydrolysis, for example oxidation, were concluded not to occur. Also, no precipitation of the cerium(IV) ion was observed during the reactions under the present conditions, though some precipitation was reported to occur in the hydrolysis of nucleoside-3',5'-cyclic monophosphates by the same catalyst.[1h]

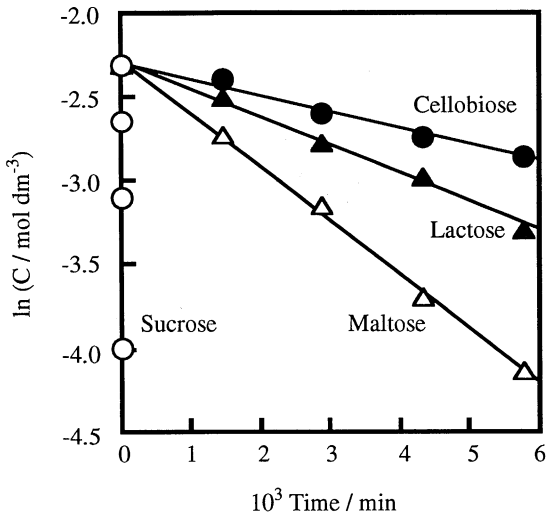


**Figure 2.** Plot of ln Conc. *vs.* time for the hydrolyses of the disaccharides by $Ce^{IV}(NH_4)_2(NO_3)_6$ (5.0 x $10^{-3}$ mol $dm^{-3}$) at pH 7.0, 100 ℃.

Time-courses of decreasing concentrations of various disaccharides in the typical experiments are shown in Figure 2. The reactions were found to proceed efficiently, for example, the sucrose hydrolysis was finished within 15 min at pH 7.0 and 100 ℃. Two features of the reactions are evident from Figure 2: (1) $Ce^{IV}(NH_4)_2(NO_3)_6$ works as a catalyst, and the turnover numbers are *ca.* 20 in the case of the sucrose and maltose hydrolyses. The reactions proceeded until the substrate was exausted, and no decomposition of the catalyst was observed before the reactions finished. The highest turnover number, 100, was attained for the hydrolysis of sucrose (0.10 mol $dm^{-3}$) by the cerium(IV) ion (1.0 x $10^{-3}$ mol $dm^{-3}$). (2) All reactions obey the first-order-reaction rate law for the concentrations of the substrates. Table 1 summarizes the first-order-reaction rate constants which were obtained in the hydrolysis of disaccharides (0.10 mol $dm^{-3}$) by the catalyst (5.0 x $10^{-3}$ mol $dm^{-3}$) at pH 7.0. The results show that the hydrolysis reactions proceed in the order of sucrose $\gg$ maltose $>$ lactose $>$ cellobiose. For the hydrolysis of sucrose which is the most favorable substrate, we examined hydrolytic activities of the lanthanoide(III) chlorides or triflates, however virtually no catalytic activities were observed. Exceptionally, $Ce^{III}(NH_4)_2(NO_3)_5$ exhibited weak hydrolytic activity, however it was remarkably smaller than that of the cerium(IV) ion (Table 1).

In the catalytic process, the cerium(IV) ion should coordinate or at least interact with the disaccharides. To investigate the intermediates, we attempted the nmr measurements of the disaccharides in the presence of the cerium(IV) ion, however we could not get useful information for the

**Table 1.** First order rate constants for hydrolysis of disaccharides by $Ce^{IV}(NH_4)_2(NO_3)_6$ at pH 7.0

| Substrate[a] | Catalyst[b] | Temp / ℃ | $10^3 k$ / $min^{-1}$ |
|---|---|---|---|
| Sucrose | $Ce^{IV}(NH_4)_2(NO_3)_6$ | 40 | 2.26 |
| Sucrose | $Ce^{IV}(NH_4)_2(NO_3)_6$ | 60 | 6.82 |
| Sucrose | $Ce^{IV}(NH_4)_2(NO_3)_6$ | 80 | 28.6 |
| Sucrose | $Ce^{IV}(NH_4)_2(NO_3)_6$ | 100 | 87.6 |
| Sucrose | $Ce^{III}(NH_4)_2(NO_3)_5$ | 100 | 1.0 |
| Sucrose | None | 100 | 0.19 |
| Maltose | $Ce^{IV}(NH_4)_2(NO_3)_6$ | 100 | 0.319 |
| Lactose | $Ce^{IV}(NH_4)_2(NO_3)_6$ | 100 | 0.17 |
| Cellobiose | $Ce^{IV}(NH_4)_2(NO_3)_6$ | 100 | 0.10 |

[a] 0.10 mol $dm^{-3}$. [b] 5.0 x $10^{-3}$ mol $dm^{-3}$.

intermediates. Next, we estimated the association constant from the Michaelis-Menten type analysis. The Michaelis-Menten constant ($K_m$) was 3.72 mol $dm^{-3}$ for the hydrolysis of sucrose at 40 ℃. Since the $K_m$ value means the substrate concentration at which the reaction rate becomes half of the maximum, the large value obtained in this work indicates that the concentrations of the intermediates were virtually negligible. This result is consistent with the literature, which describes the small association constants between the lanthanoide ions and sugars.[4]

Finally, the activation energy was determined by measuring the rate constants at 313 - 373 K. The Arrhenius plot for the hydrolysis of sucrose by the cerium(IV) ion (5.0 x $10^{-3}$ mol $dm^{-3}$) shows linear relationship (Figure 3). The activation energy ($E_a$) and the preexponential factor (A) were estimated to be 14.4 kcal $mol^{-1}$ and $10^{7.33}$ $dm^3$ $mol^{-1}$ $min^{-1}$. The $E_a$ value for hydrolysis of Sucrose by 0.18 N HCl is reported to be 30 kcal $mol^{-1}$.[5] In conclusion, $Ce^{IV}(NH_4)_2(NO_3)_6$ is a very efficient catalyst compared with an acid catalyst such as hydrochloric acid. The detailed discussions on the reaction mechanisms will appear in a succeeding paper.

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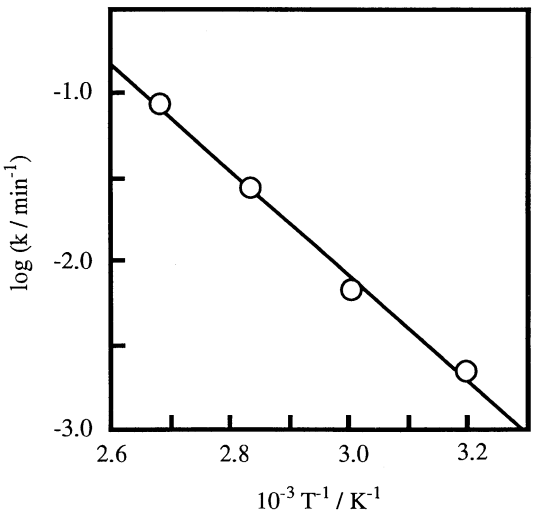


**Figure 3.** Arrhenius plot of log k vs. $T^{-1}$ for the hydrolysis of sucrose catalyzed by $Ce^{IV}(NH_4)_2(NO_3)_6$ at pH 7.0.

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