報 文

Effect of Inorganic Anions on the Catalysis in Micellar System

Cleavage of the S-S Bond in Bis(3-carboxy-4-nitrophenyl) Disulfide in the Presence of a Cationic Surfactant*

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The effect of added inorganic anions on the cleavage of S-S bond in bis (3-carboxy-4-nitrophenyl) disulfide was studied in the presence of tetradecyltrimethylammonium bromide at 25°C. The effect of retardation was in the order $\text{Cl}^- < \text{Br}^- < \text{NO}_3^-$. The effect of divalent anion SO_4^{2-} was more remarkable. The trend is in agreement with the result, for example, on the alkaline hydrolysis of *p*-nitrophenyl hexanoate in the presence of tetradecyltrimethylammonium chloride by Romsted and Cordes.

1 Introduction

It has been found in our laboratory that the cleavage of the S-S bond in bis(3-carboxy-4-nitrophenyl) disulfide (DTNB) is accelerated by the presence of the micelle of a cationic detergent, i.e., the cleavage of the S-S bond is a reaction catalyzed by the micelle of a cationic detergent¹⁾. This time studies were made on the effect of added inorganic anion on the cleavage of the S-S bond in DTNB in the presence of tetradecyltrimethylammonium bromide (TTAB).

2 Experimental

2.1 Detergent

TTAB was synthesized in our laboratory using *n*-tetradecyl alcohol which was gas-chromatographically pure. The critical micelle concentration (cmc) was determined by measuring the electric conductivity using TOA's conductometer, model CM-1DB. The cmc was 3.7×10^{-3} M in distilled water at 25°C. The value agrees with that found in the literature²⁾.

2.2 Reagents

A specially prepared DTNB was purchased from Nakarai Chemicals Ltd. This was used

without further purification. The concentration was determined assuming the molar extinction coefficient at 325 nm to be $17,500 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ³⁾. Other reagents were of the highest grade commercially available.

2.3 Basis for the Spectrophotometric Determination of the Reaction Rate

DTNB is hydrolyzed at the alkaline pH, emerging a color. Donovan and White proposed the following mechanism for the cleavage⁴⁾. Here, R represents $\text{C}_6\text{H}_4\text{NO}_2\text{COO}^-$.

If it is assumed that Eq. (1) is the rate-determining step, then $d[\text{RS}^-]/dt = k_1[\text{RS-SR}][\text{OH}^-]$. Since $[\text{OH}^-]$ is constant, Eq. (3) proceeds following the pseudo-unimolecular reaction with regard to $[\text{RS}^-]$. The RS^- anion has the absorption maximum at 412 nm and its molar extinction coefficient is $13,600 \text{ M}^{-1} \cdot \text{cm}^{-1}$ ³⁾. Thus the reaction can be followed by measuring the absorption of the system at 412 nm.

2.4 Apparatus for Measuring the Reaction Rate

Fifty ml of TTAB solution containing an

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anion and 50 ml of DTNB solution (5×10^{-5} M) were mixed; this was deaerated and then was saturated with nitrogen. The solvent was distilled water. The solution was then placed in 100 ml of four-neck flask under nitrogen atmosphere. The apparatus is shown in Fig.-1. The flask was immersed in a thermostat, the

Fig.-1 Apparatus to determine the reaction rate.

temperature of which was 25°C. Then the pH of the solution was raised and was kept at 9.2 using a pH-stat; 0.05 N KOH was supplied. The reaction mixture was circulated by use of a Peristaltic pump *via* flask $\rightarrow$ flow cell $\rightarrow$ flask. The absorbance at 412 nm was read every 5 min, and the reading was continued for 50~60 min. The reference was a mixture of DTNB, TTAB and added anion in distilled water; the composition of constituents was the same as that in the sample solution. The only difference between the reference and the sample solution was the pH.

A TOA's pH-stat model HSM-10A and TOA's pH meter model HM-20B were used. The absorption was measured by using a JASCO's spectrophotometer model UVIDE-1.

3 Results and Discussion

3.1 Rate of Hydrolysis of DTNB

Denoting the initial concentration of DTNB by a and the amount of DTNB decomposed after time t by x , $\ln \{a/(a-x)\}$ was plotted against t . Typical examples are shown in Fig.-2. Values obtained when only DTNB was present are given by the mark (●), and those obtained when TTAB was present are given by the mark (○). When there is no detergent,

Fig.-2 Cleavage of the S-S bond in DTNB, pH 9.2 and 25°C.

the reaction follows the pseudo-unimolecular reaction kinetics in 0~60 min. In contrast, the reaction is the pseudo-unimolecular reaction only at the initial stage when TTAB is present. A reason may be that the assumption that Eq. (1) is the rate-determining step is correct only at the initial stage of the reaction. The slope of the straight line gives the rate constant k_1 .

3.2 Kinetics in Micellar System

Fig.-3 shows how the rate constant k_1 changes as a function of the concentration of TTAB. The arrow in the figure indicates the

Fig.-3 Change of rate constant k_1 with the increase in the TTAB concentration, pH 9.2 and 25°C. Arrow indicates the cmc of TTAB in distilled water.

cmc of TTAB in distilled water, and accordingly its cmc in dilute KOH*. As is seen in this figure, the acceleration of the reaction

* The reaction was conducted in dilute KOH solution whose pH was 9.2. Since $[K^+] = [OH^-] = 10^{-4.8}$, the ionic strength of the KOH solution is $10^{-4.8}$ or 0.00003. Thus the cmc in this KOH solution is the same as that in distilled water.

begins at the lower concentration of cmc, attains the maximum after passing the cmc, and then decreases with the increase in the concentration of the detergent. Such a bell-shaped curve is the one characteristic to the micelle-catalyzed reaction. The maximum rate of cleavage is 10 times faster than that without TTAB.

3.3 Effect of Added Anion

Studies were made on the effect of potassium salts on the hydrolysis of DTNB in the presence of 6.8 mM of TTAB (double the cmc). Anions used were Cl^- , Br^- and NO_3^- . As is seen in Fig.-4, the rate constant k_i decreases remarkably with the increase in salt concentration.

Fig.-4 Effect of added inorganic anion on the cleavage of S-S bond in DTNB. The concentration of TTAB was 6.8 mM, pH 9.2 and 25°C.

The retardation effect of the anion is in the order: $\text{Cl}^- < \text{Br}^- < \text{NO}_3^-$. Anions I^- and SCN^- precipitated almost all the TTAB used. The series of retardation effect is in accord with the lyotropic series. Also, the series given above is in accord with that given by Romsted and Cordes⁵⁾ for the alkaline hydrolysis of *p*-nitrophenyl hexanoate in the presence of tetradecyltrimethylammonium chloride. The effect of divalent anion SO_4^{2-} is more remarkable, when its concentration is less than 50 mM.

The micelle-catalyzed reaction takes place in the Stern layer of the micelle. An interpreta-

tion for the retardation is given below. The OH^- anions locate on the micellar surface of cationic detergent. If the inorganic anions are added to the system, these anions are bound to the micellar surface, repelling OH^- anions from it. The decrease in the concentration of OH^- anion on the micellar surface is the cause of the retardation of the reaction. The stronger the force by which the anion is bound to the micellar surface, the stronger the retardation effect. Actually, the strength of the binding force was in the order of lyotropic series. Another interpretation is that the micellar structure is altered by the presence of inorganic anions⁶⁾.

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ミセル触媒反応に対する無機アニオンの影響。カチオン界面活性剤存在下でのビス(3-カルボキシ-4-ニトロフェニル)ジスルフィドのもつ S-S 結合の切断

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ビス(3-カルボキシ-4-ニトロフェニル)ジスルフィドのもつ S-S 結合の切断に対する添加無機アニオンの影響が, テトラデシルトリメチルアンモニウム=ブロミドの存在下で 25°C で調べられた。この反応を抑制する効果は $\text{Cl}^- < \text{Br}^- < \text{NO}_3^-$ の順であった。二価アニオン SO_4^{2-} の影響は 50 mM 以下ではより著しかった。この結果は, 例えば Romsted と Cordes によるテトラデシルトリメチルアンモニウム=クロリドの存在下でのヘキサノ酸 *p*-ニトロフェニルのアルカリ加水分解に対する結果と一致する。