Change in the Rate Determining Step in Hydrolysis Reaction of *N*-thenoyl-2-phenylimidazole

Jong-Pal Lee*, **Hyun-Seok Park†**, and **Tae-Seop Uhm**

Department of Chemistry, Dong-A University, Pusan 604-714, Korea
†*Division of Water Control, Hwa Myung Water Works, Pusan 614-120, Korea*
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We report a dramatic pH-rate profile for the hydrolysis of *N*-thenoyl-2-phenylimidazole which has never been observed before. The hydrolysis reactions of *N*-acylimidazoles have been actively studied in view of the similar role of histidine in biological acyl group transfer reaction.[1~10] Sometimes, these compounds give rise to exceptional hydrolytic reactivity depending on the structural features. For example, the second-order rate constant (k_{OH}) for alkaline hydrolysis of *N*-acetylimidazole is 316 $M^{-1} \cdot s^{-1}$ at 25 °C,[11] whereas k_{OH} for hydrolysis of *p*-nitrophenylacetate is only 15 $M^{-1} \cdot s^{-1}$ at the same temperature,[12] even though the pK_a value of the imidazole leaving group is 14.5,[13] while that of *p*-nitrophenol is 7.0.[12]

Recently, we reported on the hydrolysis reactions of *N*-acylimidazoles which have bulk leaving groups, such as *N*-acetyl-2,4,5-triphenylimidazole and *N*-acetyl-4,5-diphenylimidazole.[14] The rate constant for the pH-independent reaction of *N*-acetyl-4,5-diphenylimidazole was 2.0-fold larger than that of *N*-acetyl-2,4,5-triphenylimidazole and was 42-fold greater than that of *N*-acetylimidazole with the imidazole leaving group.

In this study, we have investigated the mechanism for the hydrolysis of *N*-thenoyl-2-phenylimidazole having a hetero atom in the acyl group and a phenyl group in the 2-position of the leaving group imidazole ring, which has been prepared according to a literature procedure.[15] The reaction was carried out under pseudo-first order conditions and the rates of hydrolysis of the *N*-thenoyl-2-phenylimidazole were measured spectrophotometrically in H_2O at 40 °C by following the spectral changes at 300 nm. Buffer solutions were maintained at a constant ionic strength of 0.5 M with KCl. The buffer solutions employed were formate, acetate, calcodylate, imidazole, tris, *N*-ethylmolpholine and carbonate. The hydrolysis reactions are catalyzed by buffer. Therefore, rate constants were obtained by extrapolation to zero buffer concentration.

Figure 1 is a plot of $\log k_{obs}$ at zero buffer concentration *vs* pH for hydrolysis of *N*-thenoyl-2-phenylimidazole in H_2O at 40 °C, μ=0.5 M with KCl. Hydroxide ion promoted reactions are observed at pH > 7.5. The second-order rate constant is 1320 $M^{-1} \cdot s^{-1}$. This value is about 8-fold larger than that obtained for reaction of the *N*-thenoylbenzimidazole (k_{OH}=165 $M^{-1} \cdot s^{-1}$).[16] This difference reflects that the pK_a value of the 2-phenylimidazole leaving group is smaller than that of benzimidazole.

However, the hydrolysis reactions at pH < 7 occur more complicatedly. This means that the hydrolysis reaction in this pH range is concerned with a neutral species or protonated species and should be changed the rate determining step.
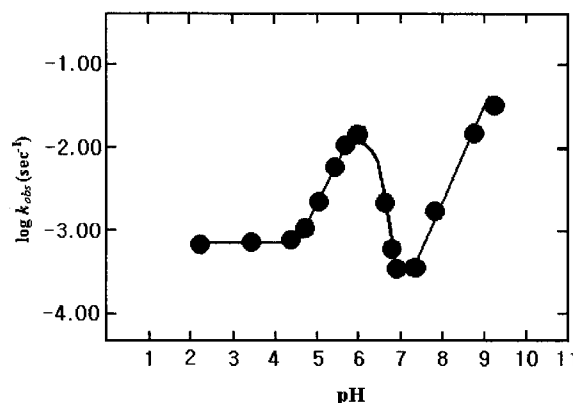

Figure 1. Plot of $\log k_{obs}$ *vs* pH for the hydrolysis of *N*-thenoyl-2-phenyl-imidazole in H_2O at 40 °C, μ=0.5 M with KCl.

As shown in Figure 1, the rate constant (k_{obs}) increases with increasing hydronium ion concentration between pH 6 and 7. This could be explained that the first protonation of the substrate(a) would be on the carbonyl oxygen. Therefore, the rate determining step, ①, would be the formation of the intermediate by attacking the water molecule on the carbonyl carbon of the protonated substrate(a) as shown in Scheme 1. In the pH range 5-6, the decrease in rate on increasing hydronium ion concentration may reflect that the proton from the intermediate(b) would be rapidly transfered to N-3 atom of the 2-phenylimidazole leaving group and then the rate determining step, ②, would be breakdown of the intermediate(c).

In contrast, almost same rate constant values with increasing hydronium ion concentration at pH < 5 could reflect that increasing the hydronium ion concentration should permit

Scheme 1

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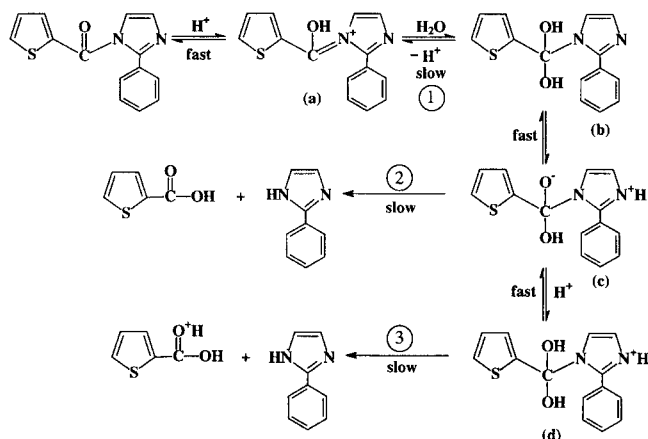
the second protonated species(d) more easily so that breakdown of the intermediate, ③, would be the rate determining step.

This result is not commonly observed in amide hydrolysis and is likely to be caused by the structural feature of the *N*-acylimidazole.

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Photoelectrochemical Stripping Behavior of Atomic Cd Layer on CdTe(100)

Mi Sun Lee, Ho Ryul Ryu, and Choong Kyun Rhee*

Department of Chemistry, Chungnam National University, Taejon 305-764, Korea
Received July 27, 1998

Recently, Stickney[1-3] has suggested a new concept of electrochemical atomic layer etching, called "electrochemical digital etching (ECDE)", to etch compound semiconductor surfaces into a depth with an atomic depth resolution. The working principle of the atomic layer manipulation was an electrochemical stripping reaction confined to surface atomic layer, which is conceptually opposite to underpotential deposition (UPD).[4] An actual atomic layer etching was examined with CdTe compound semiconductor using cyclic removal of each atomic layers of Cd and Te in a sequential manner. By setting a digital number of removal cycles, an etching depth with an atomic resolution could be achieved.

Along with ECDE, we investigated the possibility of a photoelectrochemical way to fabricate a pattern on semiconductor surfaces. The main idea of the method is projection of a light image to control the local reactivity of CdTe surface toward the atomic layer stripping reactions. To achieve the goal, the stripping behavior of Cd layers under various illumination levels was scrutinized.

A CdTe(100) crystal, purchased from II-VI Inc., was cut to a plate (25 mm × 8 mm × 0.5 mm) and polished down to 1 μm. An ohmic contact was made by rubbing indium with a

soldering iron at one end of the plate and a platinum wire (0.5 mm diameter) was soldered to it. A stoichiometric surface of the CdTe(100) electrode was prepared by chemical etching of the electrode in Br_2/MeOH solution followed by electrochemical reduction of a thick Te layer at -1.8 V.[5-7] The electrolyte used in this study was 0.1 M Na_2SO_4 (Aldrich) made from ultrapure water (> 18 MΩ) and its pH was 5.7. A light-tight box was used to control the light level reaching to the electrode. The background light was negligible. The illumination was achieved with a tungsten lamp and a halogen lamp, whose powers were ~0.1 mW/cm^2 and ~40 mW/cm^2, respectively.

A home-built potentiostat, manipulated by a computer, was used to control the potential of a conventional three-electrode system. The electrolyte was deareated with N_2 and the electrochemical cell was blanked with N_2 during the whole experiment. The reference electrode used in this work was Ag/AgCl([Cl$^-$]=1.0×10^{-5} M), but the potential reported here is against Ag/AgCl([Cl$^-$]=1.0 M).

In addition, surface analysis was performed using XPS (VG, ESCALAB 220i) for determination of relative surface concentrations of Cd and Te.

Figure 1 (a) is the cyclic voltammogram of a stoichiometric CdTe(100) surface in 0.1 M Na_2SO_4, taken in the

*Corresponding Author