

N-Arylsulfonylbenzimidothiophenyl Ester 유도체의 가수분해에 대한 반응속도론적 연구

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Kinetics and Mechanism of the Hydrolysis of *N*-Arylsulfonylbenzimidothiophenyl ester.

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요 약. 다음과 같은 새로운 4종의 *N*-(arylsulfonyl)benzamide 유도체와 6종의 *N*-(arylsulfonyl)benzimidothiophenyl ester 유도체를 합성하였다.

m-methyl-*N*-(arylsulfonyl)benzamide, *p*-methyl-*N*-(arylsulfonyl)benzamide, *m*-nitro-*N*-(arylsulfonyl)benzamide, *p*-methoxy-*N*-(arylsulfonyl)benzamide, *p*-methyl-*N*-(arylsulfonyl)benzimidothiophenyl ester, *m*-methyl-*N*-(arylsulfonyl)benzimidothiophenyl ester, *p*-methoxy-*N*-(arylsulfonyl)benzimidothiophenyl ester, *p*-nitro-*N*-(arylsulfonyl)benzimidothiophenyl ester, *m*-nitro-*N*-(arylsulfonyl)benzimidothiophenyl ester, *p*-chloro-*N*-(arylsulfonyl)benzimidothiophenyl ester.

넓은 pH 범위에서 *N*-(arylsulfonyl)benzimidothiophenyl ester 유도체의 가수분해속도 상수들 자외선 분광광도법으로 측정하여 넓은 pH 범위에 적용되는 반응속도식을 구하였다. 이속도식과 전환기효과 등으로부터 *N*-arylsulfonylbenzimidothiophenyl ester 유도체에 대한 가수분해 반응메카니즘을 제안하였다. 즉 pH 11 이상에서는 hydroxide ion 이 pH 9 이하에서는 azomethine 기에 들분자가 첨가되므로서 반응이 시작되며 pH 9~11 사이에서는 물분자와 hydroxide ion 이 경쟁적으로 반응함을 알았다.

ABSTRACT. Four unreported derivatives of *N*-arylsulfonylbenzamide and six derivatives of *N*-arylsulfonylbenzimidothiophenyl ester were prepared. These were;

p-methyl-*N*-(arylsulfonyl)benzamide, *m*-methyl-*N*-(arylsulfonyl)benzamide, *m*-nitro-*N*-(arylsulfonyl)benzamide, *p*-methoxy-*N*-(arylsulfonyl)benzamide, *p*-methyl-*N*-(arylsulfonyl)benzimidothiophenyl ester, *p*-chloro-*N*-(arylsulfonyl)benzimidothiophenyl ester, *m*-methyl-*N*-(arylsulfonyl)benzimidothiophenyl ester, *p*-nitro-*N*-(arylsulfonyl)benzimidothiophenyl ester, *m*-nitro-*N*-(arylsulfonyl)benzimidothiophenyl ester and *p*-methoxy-*N*-(arylsulfonyl)benzimidothiophenyl ester.

The rate constants of the hydrolysis of *N*-arylsulfonylbenzimidothiophenyl esters were determined by ultraviolet spectrophotometry at various pH and rate equations which can be applied over a wide pH range were obtained.

From the rate equation and substituent effects, one can conclude that above pH 11, the hydrolysis

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of *N*-arylsulfonylbenzimidothiophenyl esters are initiated by the attack of hydroxide ion, however, below pH 9, started by the addition of a water molecule on the azomethine group. At pH 9~11, the competitive reaction between a water molecule and hydroxide ion is anticipated to occur.

INTRODUCTION

The carbon-nitrogen double bond is, in many respects, intermediate between the carbon-carbon double bond and carbonyl group.¹ The addition reactions of azomethines are mainly composed of reactions in which a variety of reagents add to the polarized carbon-nitrogen double bond. Therefore, nucleophilic reagents attack the carbon atom of azomethine linkage.

During the past decade a great deal of information has appeared in the literature²⁻³ concerning the mechanism of nucleophilic addition and cleavage of the carbon-nitrogen double bond to explain a plausible mechanism in basic and neutral media, however, it has been the subject only a few kinetic studies.

Munoz and others⁴ have suggested a four center mechanism for the addition reaction of the Grignard reagent to an azomethine linkage. The kinetics of the addition of diazomethane to anils has been reported by Kadaba.⁵

Jencks and Cordes⁶ have suggested a mechanism of the hydrolysis of the Schiff bases derived from strongly basic amines such as aliphatic amines. The semilogarithmic rate-pH curve shows a bell like form under neutral and acidic condition. The portion of the curve over which the rate is independent of the pH can be explained on the basis of an attack by the hydroxide ion on the protonated Schiff base. In the case of Schiff bases derived from weakly basic aromatic amines, the expected displacement of the curve towards the lower regions of pH is observed.

Schmir⁷ has studied the kinetic behaviour of the thizolines and has led to an elaboration of the general laws which are similar to those

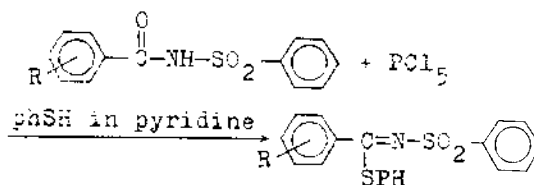
governing the hydrolysis of Schiff bases.

Ugi, Beck and Fetzer⁸ also determined the rate of hydrolysis of a series of imidoyl chloride in aqueous acetone. Electron withdrawing substituents at carbon or nitrogen generally cause a pronounced decrease in reactivity, while electron donors increase the rate of hydrolysis.

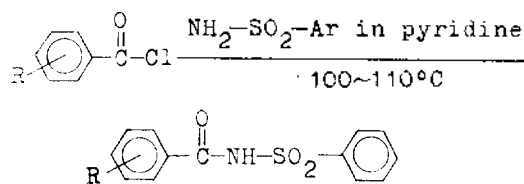
As shown in above references, some kinetic studies for the hydrolysis of the Schiff bases and the imidoyl chloride have been reported. However, the kinetic studies for the hydrolysis of the *N*-arylsulfonylbenzimidothiophenyl ester derivatives have not been reported yet.

The purpose of this investigation is to synthesize the *N*-arylsulfonylbenzimidothiophenyl ester derivatives, to determine the rate constants over a wide pH range and reveal the reaction mechanism of hydrolysis of *N*-arylsulfonylbenzimidothiophenyl ester derivatives.

The *N*-arylsulfonylbenzimidothiophenyl ester was prepared by Ishuchuk and Emelyanova⁹ from phosphorus pentachloride and *N*-arylsulfonylbenzamide via *N*-arylsulfonylbenzimidoyl chloride.



The *N*-arylsulfonylbenzamide was prepared by Crossely¹⁰⁻¹¹ by the reaction of benzoyl chloride and benzenesulfonamide as below.



EXPERIMENTAL

1. Preparation of Starting Materials.

N-Arylsulfonylbenzamide Derivatives. A 150 ml, 3-neck flask was equipped with a hook-type agitator and thermometer. Benzenesulfonamide (18.8 g, 0.12 mole) was added with 25 ml of dry pyridine. The agitator was started and the mixture heated to 90°C. Benzoyl chloride (14.1 g, 0.1 mole) was added over five minutes, in portions, via a long stemmed funnel. The flask was cooled externally to prevent the temperature from exceeding 110°C. The temperature was held at 100~110°C for fifteen minutes to complete the reaction. The resulting pyridine solution was drowned in 130 ml of 2*N* hydrochloric acid. The product, which first separated as an oil, soon crystallized into soft pellets which were filtered and washed well with water. The product was recrystallized from methanol. The yield was 15.6 g (60% calculated from benzenesulfonamide); m. p 146°C (lit.,¹² 146~147°C). Table 1 shows the analytical and spectral data of *N*-arylsulfonylbenzamide derivatives.

N-Arylsulfonylbenzimidothiophenyl ester derivatives. A mixture of 10 g *N*-arylsulfonylbenzamide (0.038 mole) and 9.36 g phosphorus

pentachloride in 30 ml of benzene was heated under reflux for 5 hrs. Then the mixture was concentrated under reduced pressure and was dissolved in 20 ml of acetone. A mixture of 4 ml of thiophenol and 4 ml of pyridine was added to the acetone solution. The reaction mixture was allowed to stand for 2 hrs and was diluted with water.

The product, which separated as an oil, soon crystallized into soft pellets. The product was recrystallized from methanol. The yield was 11.5 g (85% calculated from *N*-arylsulfonylbenzamide); m. p 91°C (lit.,⁹ 91~92°C). Table 2 shows the analytical and spectral data of *N*-arylsulfonylbenzimidothiophenyl ester derivatives.

2. Kinetics

All buffer solutions were prepared from reagent grade chemicals and distilled water. The pH of buffer solutions were confirmed by Orion Digital pH meter. The ionic strength was kept constant at 0.1 by adding sodium chloride solution. The rate vessels used were 100 ml volumetric flask in the thermostat (25°C).

At zero time, 2 ml of a freshly prepared $1.00 \times 10^{-3}M$ methanol solution of *N*-arylsulfonylbenzimidothiophenyl ester (ABTE) was pipetted into the 100 ml flask containing 98 ml of

Table 1. The result of elemental analysis and spectral data of *N*-arylsulfonylbenzamide derivative.

R-	Yield (%)	N (%)		m. p(°C)	-NH		C=O (str.)
		calcd.	found		(str.)	(bend.)	
H-	60	5.36	5.78	146(lit., ¹² 146~147)			
<i>p</i> -CH ₃ -	58	5.09	5.16	138~139	3320	1605	1662
<i>p</i> -Cl-	63	4.73	4.57	197(lit., ¹² 197~198)			
<i>m</i> -CH ₃ -	56	5.09	5.21	113	3250	1600	1680
<i>p</i> -NO ₂ -	65	9.15	9.68	215(lit., ¹² 216~217)			
<i>m</i> -NO ₂ -	60	9.15	9.27	191~192	3250	1614	1700
<i>p</i> -CH ₃ O-	55	4.81	4.76	139~140	3280	1590	1670

Table 2. The analytical and spectral data of *N*-arylsulfonylbenzimidothiophenyl ester derivative.

R-	yield(%)	N(%)		m. p(°C)	—C=N—(str.)
		calcd.	found		
H-	85	3.95	3.87	91 (lit., ⁹ 91~92)	
<i>p</i> -CH ₃ -	80	3.80	3.86	110	1550
<i>p</i> -Cl-	83	3.62	3.74	112~113	1555
<i>m</i> -CH ₃ -	79	3.80	3.97	110	1550
<i>p</i> -NO ₂ -	85	7.03	6.92	167~168	1555
<i>m</i> -NO ₂ -	85	7.03	6.83	126	1555
<i>p</i> -CH ₃ O-	80	3.65	3.75	139~140	1560

Table 3. The molar absorptivities(ϵ) of *N*-(arylsulfonyl)benzimidothiophenyl ester(ABTE) derivatives and *N*-(arylsulfonyl) benzamide (ABA) derivatives at various wave length.

	270 nm	290 nm	305 nm
<i>p</i> -NO ₂ ABTE	2.06×10^4 (max)	1.53×10^4	7.90×10^3
<i>p</i> -NO ₂ ABA	1.69×10^4	1.35×10^4	7.90×10^3
<i>m</i> -NO ₂ ABTE	2.11×10^4 (max)	1.20×10^4	6.20×10^3
<i>m</i> -NO ₂ ABA	1.16×10^4	4.50×10^3	1.90×10^3
<i>p</i> -Cl ABTE	1.40×10^4 (max)	1.17×10^4	6.60×10^3
<i>p</i> -Cl ABA	7.90×10^3	5.00×10^2	4.00×10^2
<i>p</i> -CH ₃ ABTE	1.26×10^4 (max)	1.07×10^4	7.00×10^3
<i>p</i> -CH ₃ ABA	6.70×10^3	4.00×10^2	0
<i>m</i> -CH ₃ ABTE	7.10×10^3 (max)	5.40×10^3	3.20×10^3
<i>m</i> -CH ₃ ABA	3.30×10^3	9.00×10^2	0
<i>p</i> -CH ₃ OABTE	1.15×10^4	1.46×10^4	3.10×10^4 (max)
<i>p</i> -CH ₃ OABA	2.09×10^4	4.00×10^3	0
ABTE	1.15×10^4 (max)	8.60×10^3	4.00×10^3
ABA	3.80×10^3	2.00×10^2	0

buffer solution.

The optical density of ABTE derivatives was determined on a Perkin-Elmer UV-Vis Spectrophotometer. The hydrolysis product of ABTE was identified as *N*-arylsulfonylbenzamide by Ishuchuk and Emelyanova.⁹ Since the molar absorptivities of *N*-arylsulfonylbenzamide(ABA) derivatives were negligible comparing those of ABTE derivatives as shown in Table 3, the optical density of H-, *m*-CH₃-, *p*-CH₃ and *p*-CH₃O-ABTE were determined at 305 nm. The optical density of *p*-Cl- and *m*-NO₂-ABTE were

determined at 290 nm and *p*-NO₂-ABTE was determined at 270 nm.

RESULT and DISCUSSION

The initial concentrations of ABTE derivatives ($2.00 \times 10^{-4} M$) were kept constant over wide pH range. A logarithmic plot of optical density (OD) vs. time at pH 4.00 and 25°C, as shown in Fig. 1 gives a straight line. Fig. 2 is a logarithmic plot of $(a-x)$ vs. time showing the

absorbance of hydrolysis of *p*-NO₂ ABTE is not negligible. Where *a* is the initial concentration of ABTE derivative and *x* is the concentration of ABA derivative with time.

The first order rate constants (*k_t*) calculated from the straight line of various pH are given in Table 4~10 and Fig. 3~9 show pH rate profile of these reactions. As shown in Fig. 3~6 the change of log *k_t* remains constant and above pH 11.00, the slope is 1.0, i.e., *k_t* is directly proportional to the hydroxide ion concentration.

Fig. 3 shows the logarithmic plot of *k_t* against pH for the hydrolysis of ABTE. Analysis of Fig. 3 shows that the total rate constant *k_t* is given by an expression of the form

$$k_t = k_{10} + k_1^{OH} OH^- \quad (1)$$

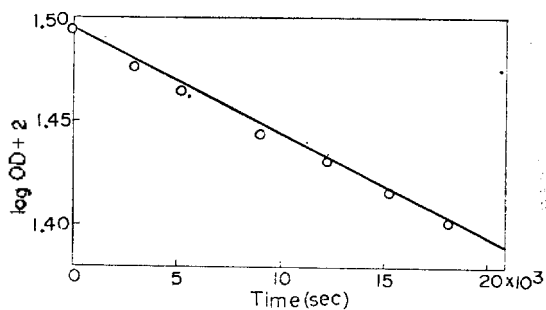


Fig. 1. The plots of log (ABTE) vs. time at pH 4.00 and 25°C

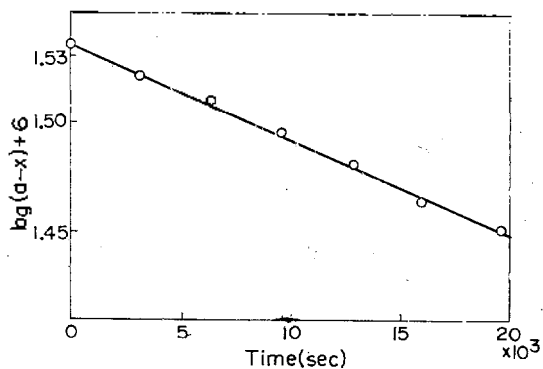
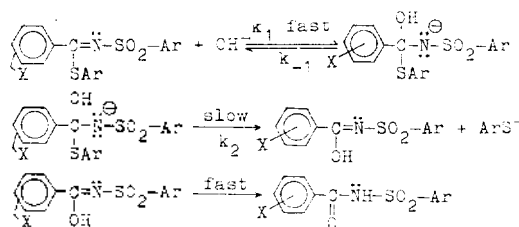


Fig. 2. The plots of log (*p*-NO₂ AB5TE) vs. time at pH 4.00 and 25°C

The last term in equation 1 is the nucleophilic addition constant of hydroxide ion on azomethine group.¹³⁻¹⁴ Above pH 11.00, the rate of this reaction is proportional to hydroxide ion concentration.

Therefore, the mechanism of hydrolysis in basic media is,



Willi¹⁵ suggested that in the case of aliphatic Schiff base hydrolysis the reaction involves first protonation and then attacks of hydroxide ion on the protonated Schiff base in alkaline media. Therefore the rate of hydrolysis remains constant independent of the pH. But the rate of aromatic Schiff base hydrolysis increases at a rate proportional of the concentration of hydroxide ion by the effect of phenyl group without being protonated.¹⁶ This suggests that the imine-carrying carbon atom of ABTE is sufficiently positive to undergo attack by the hydroxide ion.

In this mechanism, however, it does not show whether the rate determining stage is the first step in which the hydroxide ion is added or it is the second step in which the thiophenyl group is eliminated. Actually the ρ value equal

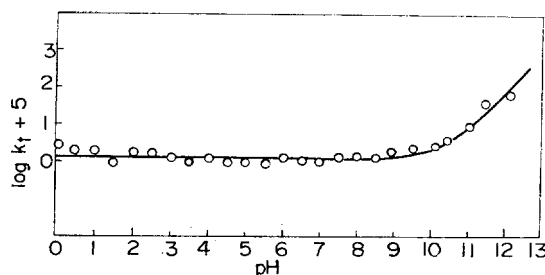


Fig. 3. pH-rate profile for the hydrolysis of N-(arylsulfonyl)benzimidothiophenyl ester at 25°C.

Table 4. Rate constants for the hydrolysis of ABTE at various pH & 25 °C.

Buffer solution	pH	k_t (sec ⁻¹)	
		Observed	Calculated
HCl	0.00	3.10×10^{-5}	1.44×10^{-5}
	0.50	1.82×10^{-5}	1.44×10^{-5}
	1.00	1.77×10^{-5}	1.44×10^{-5}
	1.50	1.08×10^{-5}	1.44×10^{-5}
	2.00	1.72×10^{-5}	1.44×10^{-5}
	2.50	1.72×10^{-5}	1.44×10^{-5}
	3.00	1.18×10^{-5}	1.44×10^{-5}
HAc+NaAc	3.50	1.08×10^{-5}	1.44×10^{-5}
	4.00	1.15×10^{-5}	1.44×10^{-5}
	4.50	1.53×10^{-5}	1.44×10^{-5}
	5.00	1.04×10^{-5}	1.44×10^{-5}
	5.50	1.02×10^{-5}	1.44×10^{-5}
	6.00	1.15×10^{-5}	1.44×10^{-5}
KH ₂ PO ₄ +K ₂ HPO ₄	6.50	1.14×10^{-5}	1.44×10^{-5}
	7.00	1.10×10^{-5}	1.44×10^{-5}
	7.50	1.11×10^{-5}	1.44×10^{-5}
	8.00	1.15×10^{-5}	1.44×10^{-5}
Boric acid+NaOH	8.50	1.64×10^{-5}	1.46×10^{-5}
	9.00	1.82×10^{-5}	1.51×10^{-5}
	9.50	2.02×10^{-5}	1.67×10^{-5}
	10.00	3.00×10^{-5}	2.12×10^{-5}
	10.50	3.12×10^{-5}	3.74×10^{-5}
	11.00	9.87×10^{-5}	8.24×10^{-5}
	11.50	3.20×10^{-4}	2.34×10^{-4}
NaOH	12.00	7.10×10^{-4}	6.74×10^{-4}

Table 5. Rate constants for the hydrolysis of *p*-CH₃ABTE at various pH & 25 °C.

Buffer solution	pH	k_t (sec ⁻¹)	
		Observed	Calculated
HCl	0.00	6.87×10^{-5}	3.53×10^{-5}
	0.50	4.02×10^{-5}	2.53×10^{-5}
	1.00	3.17×10^{-5}	3.53×10^{-5}
	1.50	3.07×10^{-5}	3.53×10^{-5}
	2.00	3.45×10^{-5}	3.53×10^{-5}
	2.50	3.27×10^{-5}	3.53×10^{-5}
	3.00	3.02×10^{-5}	3.53×10^{-5}
	HAc+NaAc	3.50	3.14×10^{-5}
4.00		2.93×10^{-5}	3.53×10^{-5}
4.50		3.78×10^{-5}	3.53×10^{-5}
5.00		3.26×10^{-5}	3.53×10^{-5}

	5.50	2.57×10^{-5}	3.53×10^{-5}
	6.00	3.68×10^{-5}	3.53×10^{-5}
KH ₂ PO ₄ +K ₂ HPO ₄	6.50	3.21×10^{-5}	3.53×10^{-5}
	7.00	4.06×10^{-5}	3.53×10^{-5}
	7.50	3.42×10^{-5}	3.53×10^{-5}
	8.00	3.30×10^{-5}	3.32×10^{-5}
Boric acid+NaOH	8.50	3.29×10^{-5}	3.36×10^{-5}
	9.00	3.59×10^{-5}	3.72×10^{-5}
	9.50	4.94×10^{-5}	4.13×10^{-5}
	10.00	6.96×10^{-5}	5.47×10^{-5}
	10.50	1.26×10^{-4}	9.70×10^{-5}
	11.00	2.52×10^{-4}	2.29×10^{-4}
	11.50	7.10×10^{-4}	6.55×10^{-4}
	12.00	2.00×10^{-3}	1.97×10^{-3}
NaOH	12.50	8.82×10^{-3}	6.23×10^{-3}

Table 6. Rate constants hydrolysis of *m*-methyl-*N*-(arylsulfonyl)benzimidothiophenyl ester at various pH & 25 °C.

Buffer Solution	pH	k_f (sec ⁻¹)	
		Observed	Calculated
HCl	0.00	4.82×10^{-5}	1.70×10^{-5}
	0.50	2.30×10^{-5}	1.70×10^{-5}
	1.00	1.70×10^{-5}	1.70×10^{-5}
	1.50	1.36×10^{-5}	1.70×10^{-5}
	2.00	1.30×10^{-5}	1.70×10^{-5}
	2.50	1.32×10^{-5}	1.70×10^{-5}
	3.00	1.43×10^{-5}	1.70×10^{-5}
HAc+NaAc	3.50	1.26×10^{-5}	1.70×10^{-5}
	4.00	1.18×10^{-5}	1.70×10^{-5}
	4.50	1.27×10^{-5}	1.70×10^{-5}
	5.00	1.37×10^{-5}	1.70×10^{-5}
	5.50	1.20×10^{-5}	1.70×10^{-5}
	6.00	1.05×10^{-5}	1.70×10^{-5}
KH ₂ PO ₄ +K ₂ HPO ₄	6.50	1.40×10^{-5}	1.70×10^{-5}
	7.00	1.40×10^{-5}	1.70×10^{-5}
	7.50	1.20×10^{-5}	1.70×10^{-5}
	8.00	1.25×10^{-5}	1.70×10^{-5}
Boric acid+NaOH	8.50	1.40×10^{-5}	1.72×10^{-5}
	9.00	1.80×10^{-5}	1.80×10^{-5}
	9.50	2.00×10^{-5}	2.00×10^{-5}
	10.00	2.57×10^{-5}	2.80×10^{-5}
	10.50	3.10×10^{-5}	4.18×10^{-5}
	11.00	6.21×10^{-5}	8.14×10^{-5}
	11.50	2.20×10^{-4}	2.05×10^{-4}

	12.00	5.70×10^{-4}	5.89×10^{-4}
NaOH	12.50	2.10×10^{-3}	1.83×10^{-3}

Table 7. Rate constants for the hydrolysis of *p*-chloro ABTE at various pH & 25 °C.

Buffer Solution	pH	k_t (sec ⁻¹)	
		Observed	Calculated
HCl	0.00	5.06×10^{-5}	2.00×10^{-5}
	0.50	2.50×10^{-5}	2.00×10^{-5}
	1.00	2.00×10^{-5}	2.00×10^{-5}
	1.50	1.00×10^{-5}	2.00×10^{-5}
	2.00	1.50×10^{-5}	2.00×10^{-5}
	2.50	1.60×10^{-5}	2.00×10^{-5}
	3.00	1.00×10^{-5}	2.00×10^{-5}
HAc+NaAc	3.50	1.30×10^{-5}	2.00×10^{-5}
	4.00	1.40×10^{-5}	2.00×10^{-5}
	4.50	1.30×10^{-5}	2.00×10^{-5}
	5.00	1.40×10^{-5}	2.00×10^{-5}
	5.50	1.20×10^{-5}	2.00×10^{-5}
	6.00	1.60×10^{-5}	2.00×10^{-5}
K ₂ HPO ₄ +KH ₂ PO ₄	6.50	2.00×10^{-5}	2.00×10^{-5}
	7.00	1.40×10^{-5}	2.00×10^{-5}
	7.50	1.60×10^{-5}	2.00×10^{-5}
	8.00	1.20×10^{-5}	2.03×10^{-5}
Boric acid+NaOH	8.50	2.00×10^{-5}	2.14×10^{-5}
	9.00	2.20×10^{-5}	2.34×10^{-5}
	9.50	2.50×10^{-5}	2.79×10^{-5}
	10.00	3.60×10^{-5}	3.84×10^{-5}
	10.50	4.30×10^{-5}	7.94×10^{-5}
	11.00	1.30×10^{-4}	1.65×10^{-4}
	11.50	3.50×10^{-4}	4.49×10^{-4}
	12.00	1.40×10^{-3}	1.43×10^{-3}
NaOH	12.50	5.01×10^{-3}	4.46×10^{-3}

Table 8. Rate constants for the hydrolysis of *p*-methoxy ABTE at various pH & 25 °C.

Buffer Solution	pH	k_t (sec ⁻¹)	
		Observed	Calculated
HCl	0.00	4.15×10^{-5}	3.68×10^{-5}
	0.50	2.76×10^{-5}	3.68×10^{-5}
	1.00	2.76×10^{-5}	3.68×10^{-5}
	1.50	2.76×10^{-5}	3.68×10^{-5}
	2.00	2.30×10^{-5}	3.68×10^{-5}
	2.50	2.30×10^{-5}	3.68×10^{-5}

	3.00	2.30×10^{-5}	3.68×10^{-5}
HAc+NaAc	3.50	2.25×10^{-5}	3.68×10^{-5}
	4.00	3.84×10^{-5}	3.68×10^{-5}
	4.50	3.87×10^{-5}	3.68×10^{-5}
	5.00	4.08×10^{-5}	3.68×10^{-5}
	5.50	3.45×10^{-5}	3.68×10^{-5}
	6.00	3.38×10^{-5}	3.68×10^{-5}
KH ₂ PO ₄ +K ₂ HPO ₄	6.50	4.61×10^{-5}	3.68×10^{-5}
	7.00	5.12×10^{-5}	3.68×10^{-5}
	7.50	4.89×10^{-5}	3.68×10^{-5}
	8.00	4.76×10^{-5}	3.73×10^{-5}
Boric acid+NaOH	8.50	5.14×10^{-5}	3.80×10^{-5}
	9.00	5.45×10^{-5}	4.06×10^{-5}
	9.50	6.00×10^{-5}	4.68×10^{-5}
	10.00	6.14×10^{-5}	7.51×10^{-5}
	10.50	1.92×10^{-4}	1.56×10^{-4}
	11.00	3.45×10^{-4}	4.19×10^{-4}
	11.50	1.15×10^{-3}	1.21×10^{-3}
	12.00	3.84×10^{-3}	3.86×10^{-3}
NaOH	12.50	6.62×10^{-3}	1.21×10^{-2}

Table 9. Rate constants for the hydrolysis of *p*-nitro ABTE at various pH & 25 °C.

Buffer Solution	pH	k_t (sec ⁻¹)	
		Observed	Calculated
HCl	0.00	9.87×10^{-8}	9.90×10^{-8}
	0.50	1.01×10^{-7}	9.90×10^{-8}
	1.00	1.10×10^{-7}	9.90×10^{-8}
	1.50	9.96×10^{-8}	9.90×10^{-8}
			9.90×10^{-8}
	2.50	1.00×10^{-7}	9.90×10^{-8}
	3.00	1.06×10^{-7}	9.90×10^{-8}
HAc+NaAc	3.50	1.10×10^{-7}	9.90×10^{-8}
	4.00	9.97×10^{-8}	9.90×10^{-8}
	4.50	1.15×10^{-7}	9.90×10^{-8}
	5.00	1.11×10^{-7}	9.90×10^{-8}
	5.50	1.17×10^{-7}	9.90×10^{-8}
	6.00	1.02×10^{-7}	9.90×10^{-8}
K ₂ HPO ₄ +KH ₂ PO ₄	6.50	1.16×10^{-7}	9.90×10^{-8}
	7.00	1.16×10^{-7}	1.00×10^{-7}
	7.50	1.13×10^{-7}	1.00×10^{-7}
	8.00	1.11×10^{-7}	1.05×10^{-7}
Boric acid+NaOH	8.50	1.16×10^{-7}	1.07×10^{-7}
	9.00	1.20×10^{-7}	1.26×10^{-7}
	9.50	1.60×10^{-7}	1.79×10^{-7}

	10.00	1.78×10^{-7}	1.90×10^{-7}
	10.50	3.45×10^{-7}	3.91×10^{-7}
	11.00	1.35×10^{-6}	1.40×10^{-6}
	11.50	3.57×10^{-6}	3.89×10^{-6}
	12.00	1.11×10^{-5}	1.25×10^{-5}
NaOH	12.50	4.40×10^{-5}	3.89×10^{-5}
	13.00	1.21×10^{-4}	1.23×10^{-4}
	13.50	5.42×10^{-4}	3.89×10^{-4}

Table 10. Rate constants for the hydrolysis of *m*-nitro ABTE at various pH & 25 °C.

Buffer Solution	pH	k_t (sec ⁻¹)	
		Observed	Calculated
HCl	0.00	2.19×10^{-7}	2.19×10^{-7}
	0.50	1.85×10^{-7}	2.19×10^{-7}
	1.00	1.61×10^{-7}	2.19×10^{-7}
	1.50	2.02×10^{-7}	2.19×10^{-7}
	2.00	2.21×10^{-7}	2.19×10^{-7}
	2.50	2.16×10^{-7}	2.19×10^{-7}
	3.00	1.97×10^{-7}	2.19×10^{-7}
HAc+NaAc	3.50	2.10×10^{-7}	2.19×10^{-7}
	4.00	2.13×10^{-7}	2.19×10^{-7}
	4.50	2.06×10^{-7}	2.19×10^{-7}
	5.00	2.12×10^{-7}	2.19×10^{-7}
	5.50	2.26×10^{-7}	2.19×10^{-7}
	6.00	2.56×10^{-7}	2.19×10^{-7}
KH ₂ PO ₄ +K ₂ HPO ₄	6.50	2.43×10^{-7}	2.19×10^{-7}
	7.00	2.38×10^{-7}	2.19×10^{-7}
	7.50	2.17×10^{-7}	2.19×10^{-7}
	8.00	2.51×10^{-7}	2.19×10^{-7}
Boric acid+NaOH	8.50	2.67×10^{-7}	2.83×10^{-7}
	9.00	3.21×10^{-7}	3.20×10^{-7}
	9.50	4.26×10^{-7}	5.00×10^{-7}
	10.00	5.18×10^{-7}	7.90×10^{-7}
	10.50	7.67×10^{-7}	1.00×10^{-6}
	11.00	3.12×10^{-6}	3.71×10^{-6}
	11.50	5.76×10^{-6}	1.00×10^{-5}
	12.00	3.25×10^{-5}	3.25×10^{-5}
NaOH	12.50	6.33×10^{-5}	1.00×10^{-4}
	13.00	3.20×10^{-4}	3.20×10^{-4}
	13.50	7.83×10^{-4}	1.00×10^{-3}

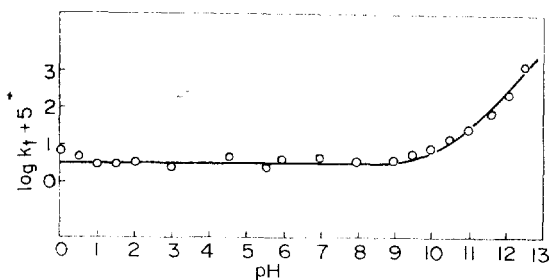


Fig. 4. pH-rate profile for the hydrolysis of *p*-methyl-*N*-(arylsulfonyl)benzimidothiophenyl ester at 25°C.

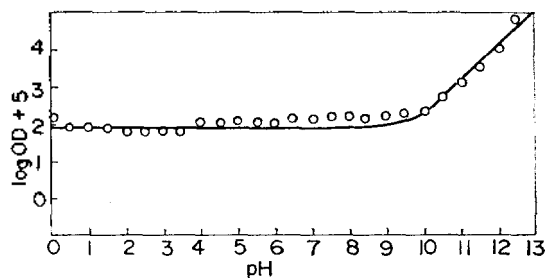


Fig. 7. pH-rate profile for the hydrolysis of *p*-methoxy-*N*-(arylsulfonyl)benzimidothiophenyl ester at 25°C.

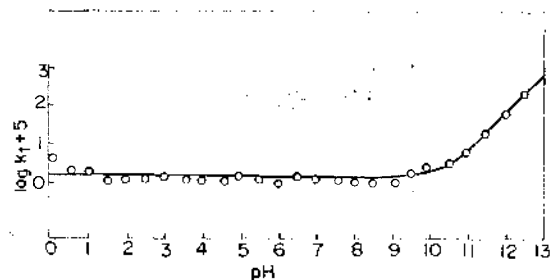


Fig. 5. pH-rate profile for the hydrolysis of *m*-methyl-*N*-(arylsulfonyl)benzimidothiophenyl ester at 25°C.

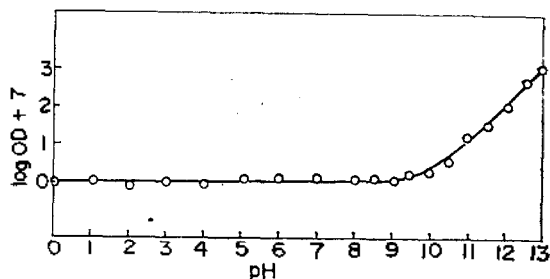


Fig. 8. pH-rate profile for the hydrolysis of *p*-nitro-*N*-(arylsulfonyl)benzimidothiophenyl ester at 25°C.

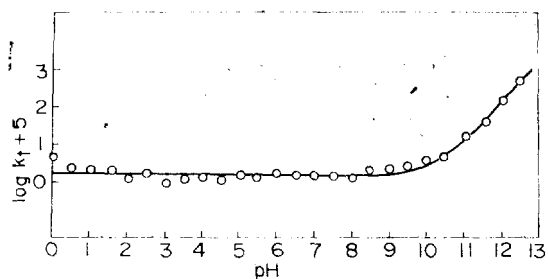


Fig. 6. pH-rate profile for the hydrolysis of *p*-chloro-*N*-(arylsulfonyl)benzimidothiophenyl ester at 25°C.

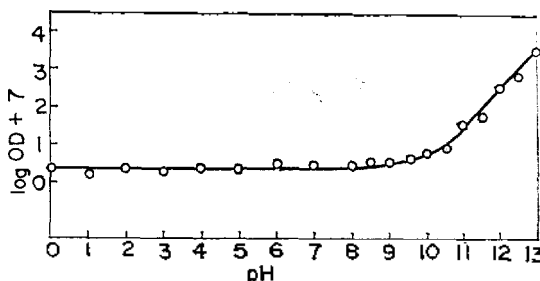


Fig. 9. pH-rate profile for the hydrolysis of *m*-nitro-*N*-(arylsulfonyl)benzimidothiophenyl ester at 25°C.

to -2.25 obtained from the Hammett plots^{17,18} at pH 12.00 as shown in Fig. 11 and it is demonstrated that the second step is rate determining stage. Further evidence in favour of this mechanism can be obtained from the study of hydrolysis of ABTE which has the various substituents in thiophenyl group.

At pH 0.00~9.00, water molecule would be

added to the ABTE by the effect of benzenesulfonyl group without being protonated. Therefore, the rate (k_t) of this reaction remains constant independent of pH and the following mechanism is proposed.

Fig. 10 shows that the hydrolysis of ABTE is not catalyzed by the general base. This suggests the fact that the second step is not rate deter-

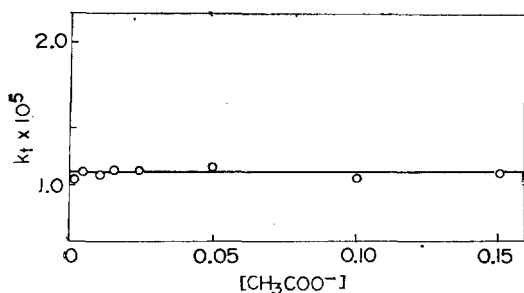


Fig. 10. General base catalyzed hydrolysis of *N*-(arylsulfonyl)benzimidothiophenyl ester at pH 4.65 and 25 °C.

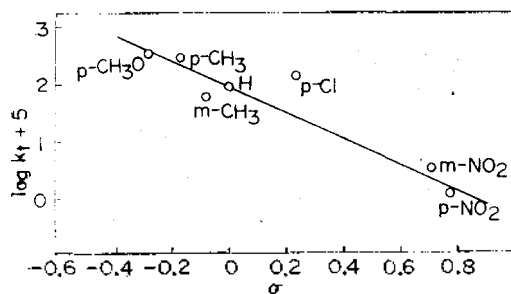
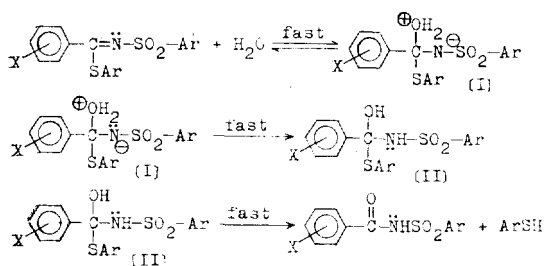


Fig. 11. Logarithmic plot of the rate of hydrolysis of *N*-(arylsulfonyl)-benzimidothiophenyl ester derivatives at pH 12 against Hammett's σ function.



mining stage. It is assumed that the deprotonation of oxonium ion (formular 1) in the second step occurred fast by the negatively charged nitrogen atom.¹³⁻¹⁴ Fig. 12 shows the Hammett plots of ABTE at pH 4.00. The ρ value equal to -2.25 demonstrated that the third step determining stage. The plots of $\log k_t$ against σ exhibits a large ρ value, thus indicating the

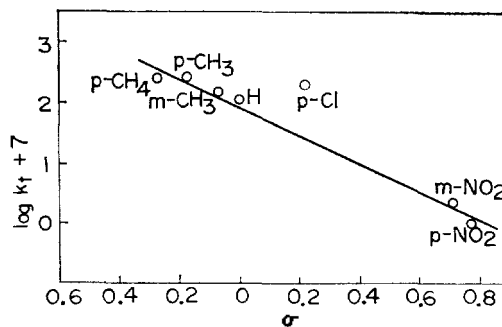


Fig. 12. Logarithmic plot of the rate of hydrolysis of *N*-(arylsulfonyl)benzimidothiophenyl ester derivatives at pH 4.00 against Hammett's σ function.

sensitivity of the reaction to substituent effects. The formation of the intermediate carbinolamine such as formular(11) has already been proposed by the work of Jencks¹⁹⁻²⁰ in the case of Schiff base hydrolysis.

At pH 0.00~9.00 k_{10} , takes 1.44×10^{-5} which is the average value of observed rate constants. The value of k_1^{OH} is obtained from the slope of the straight line in Fig. 3. The nucleophilic addition constant for hydroxide ion $k_1^{\text{OH}} = 6.80 \times 10^{-2} \text{ sec}^{-1}$ is determined from the value of $k_t = 9.87 \times 10^{-5} \text{ sec}^{-1}$ at pH 11.00 and $k_t = 7.10 \times 10^{-4}$ at pH 12.00.

As a result, over-all rate constant becomes

$$\begin{aligned}
 k_t &= 1.44 \times 10^{-5} + 6.80 \times 10^{-2} [\text{OH}^-] \\
 &= 1.44 \times 10^{-5} + 6.80 \times 10^{-16} / [\text{H}^+] \quad (2)
 \end{aligned}$$

Fig. 3 and Table 4 show that that the values of over-all rate constant, k_t calculated by equation (2). The values of calculated k_t are in good agreement with the observed.

From the rate equation, the mechanism of hydrolysis of ABTE over wide pH range is fully explained; below pH 9.00, water is added to ABTE and at pH 9.00~11.00, water and hydroxide ion competitively added to ABTE and as the pH is increased, the portion of the more reactive hydroxide ion addition is increased.

Similarly, the following rate equation for the

hydrolysis of ABTE derivatives are obtained;

$$p\text{-CH}_3\text{-ABTE} \quad k_t = 3.53 \times 10^{-5} + 1.94 \times 10^{-15}/[\text{H}^+] \quad (3)$$

$$m\text{-CH}_3\text{-ABTE} \quad k_t = 1.70 \times 10^{-5} + 5.64 \times 10^{-16}/[\text{H}^+] \quad (4)$$

$$p\text{-Cl-ABTE} \quad k_t = 2.00 \times 10^{-5} + 1.41 \times 10^{-15}/[\text{H}^+] \quad (5)$$

$$p\text{-CH}_3\text{O-ABTE} \quad k_t = 3.68 \times 10^{-5} + 3.83 \times 10^{-15}/[\text{H}^+] \quad (6)$$

$$p\text{-NO}_2\text{-ABTE} \quad k_t = 9.90 \times 10^{-5} + 1.23 \times 10^{-17}/[\text{H}^+] \quad (7)$$

$$m\text{-NO}_2\text{-ABTE} \quad k_t = 2.19 \times 10^{-7} + 3.20 \times 10^{-17}/[\text{H}^+] \quad (8)$$

Since the rate of hydrolysis of ABTE is accelerated by the electron donating group with $\rho = -2.25$, the elimination step of thiophenyl group is rate determining. The similarity of $\rho = -2.25$ at pH 4.00 and pH 12.00 accounts for the reaction mechanism remains constant at different pH.

It is of interest that the rate constants increased slightly depending on the hydrogen ion concentration at pH 0~1 but further investigation for the hydrolysis in strong acidic media is obviously desirable.

CONCLUSION

1. Four new derivatives of *N*-arylsulfonylbenzamide and six derivatives of *N*-arylsulfonylbenzimidothiophenyl ester were prepared.

2. The kinetics of the hydrolysis of the ABTE derivatives over wide pH range was presented and analyzed in detail. The rate equations which can be applied over wide pH range are as follows:

$$\begin{aligned} \text{ABTE} \quad k_t &= 1.44 \times 10^{-5} + 6.80 \times 10^{-16}/[\text{H}^+] \\ p\text{-CH}_3\text{ABTE} \quad k_t &= 3.53 \times 10^{-5} + 1.94 \times 10^{-15}/[\text{H}^+] \\ m\text{-CH}_3\text{ABTE} \quad k_t &= 1.70 \times 10^{-5} + 5.64 \times 10^{-16}/[\text{H}^+] \\ p\text{-CH}_3\text{OABTE} \quad k_t &= 3.68 \times 10^{-5} + 3.83 \times 10^{-15}/[\text{H}^+] \\ p\text{-Cl ABTE} \quad k_t &= 2.00 \times 10^{-5} + 1.41 \times 10^{-15}/[\text{H}^+] \end{aligned}$$

$$\begin{aligned} p\text{-NO}_2\text{ABTE} \quad k_t &= 9.90 \times 10^{-5} + 1.23 \times 10^{-17}/[\text{H}^+] \\ m\text{-NO}_2\text{ABTE} \quad k_t &= 2.17 \times 10^{-7} + 3.20 \times 10^{-17}/[\text{H}^+] \end{aligned}$$

3. From the rate equations obtained the mechanism of hydrolysis of the ABTE derivative over wide pH range is fully explained; below pH 9.00, water is added to ABTE derivative and at pH 9.00~11.00, water and hydroxide ion competitively added to ABTE derivative, however, above pH 11, the hydrolysis is proceeded only by the attack of hydroxide ion on the azomethine group.

The elimination step of thiophenyl group is the rate determining stage for the hydrolysis of ABTE derivative, since the rate is increased with the electron donating group with $\rho = -2.25$ at pH 12.00 and 4.00.

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