Kinetics and Mechanism of the Hydrolysis of N-(Benzenesulfonyl) benzimidoyl Chlorides

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The rates of hydrolysis of N-(benzenesulfonyl) benzimidoyl chlorides (p-H, p-CH$_3$, p-CH$_3$, p-NO$_2$ and m-NO$_2$) have been measured by UV spectrometry in 60% methanol-water at 25 °C and a rate equation which can be applied over wide pH range was obtained. Below pH 7.00, the substituent effect on the hydrolysis rate of N-(benzenesulfonyl) benzimidoyl chloride was found to conform to the Hammett σ constant with $\rho = -0.91$, whereas above pH 9.00, with $\rho = 0.94$. On the basis of the rate equation obtained and the effect of solvent, substituents and salt, the following reaction mechanism were proposed; below pH 7.00, the hydrolysis of N-(benzenesulfonyl) benzimidoyl chloride proceeds by S_N1 mechanism, however, above pH 9.00, the hydrolysis is initiated by the attack of the hydroxide ion and in the range of pH 7.00-9.00, these two reactions occur competitively.

Introduction

The reactivity of azomethines having 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.

In general, when electron withdrawing substituents exist at carbon atom of azomethines, nucleophilic substitution reaction occurs on carbon atom. Although azomethines such as imidoyl halides and hydrazidic halides have been widely used as intermediates in many organic syntheses,[2] especially, heterocyclic compound synthesis[3-8], the reaction has been the subject of only a few kinetic studies.

Moreover, the mechanism of substitution of halides in carbon-nitrogen double bond system (I) is less well understood.[9-12]

$$\underset{(I)}{\overset{\displaystyle \overset{\text{Cl}}{|}}{\text{Ar}^{1}-\text{N}=\text{C}-\text{Ar}^{2}}}$$
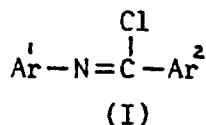
Scott and others[13] have reported that the mechanism of the hydrolysis of N-arylhydrazidic bromide in 80% aqueous dioxane are explained in terms of S_N1 mechanism involving azocarbonium ion.

Kim and others[14] revealed that the kinetics of hydrolysis of N-(p-nitrophenyl) benzohydrazonyl bromide in 60% dioxane-water at 25 °C are rationalized in terms of S_N1 and S_N2 mechanism.

Hegarty, Cronin and Scott[15] have investigated that the mechanism of the hydrolysis of N-arylbenzimidoyl chloride in 90% aqueous dioxane at 25 °C occurs by a unimolecular mechanism over the pH range 0—14. Also, they showed that in neutral solution the stabilized carbonium ion are formed from salt and common ion effects and solvent effects.

Ugi, Beck and Fetzer[16] has been studied the kinetics of hydrolysis of imidoyl chloride derivatives in aqueous acetone. They have suggested a two step mechanism involving a nitrilium ion pair intermediate.

As shown in above references, some kinetic studies for

Table 1. Analytical and spectral data of N-(benzenesulfonyl)-benzimidoyl chloride derivatives

R-	m.p.	λ_{max} (nm)	ε_{max}	Cl(%) calcd.	Cl(%) found	C=N (str.) (cm^{-1})	yield (%)
p-H	81	273	1.47×10^4	12.70	12.00	1595	85
p-CH$_3$	83	290	8.78×10^4	10.91	10.72	1590	80
p-CH$_3$O	76	292	9.24×10^4	10.91	10.80	1595	82
p-NO$_2$	116	268	1.50×10^4	12.06	11.50	1595	90
m-NO$_2$	102	267	1.20×10^4	11.44	1600		86

the substitution of halides have been reported. However, the kinetic studies for the hydrolysis of the N-(benzenesulfony) benzimidoyl chloride derivatives have not reported yet.

Experimental

N-(Benzenesulfonyl)benzimidoyl chloride (BBIC) was prepared from N-(benzenesulfonyl)benzamide and phosphorus pentachloride.[17] Recrystallization of the crude material from carbon tetrachloride and ether yielded white product, m.p. 81 °C (lit.[18], 81–82°C). Other derivatives of BBIC was also prepared by previous method.

Table 1 shows the analytical and spectral data of N-(benzenesulfonyl)benzimidoyl chloride derivatives.

Reagents used and all buffer solutions were prepared from reagent grade chemicals (Merck). The pH of buffer solution was confirmed by Radiometer pH meter 29 (Denmark Copenhagen) and the ionic strength was kept constant at 0.10 by adding sodium chloride solution.

The rate vessels used were 100 m*l* volumetric flasks and kinetic runs were made in water at 25 °C. At zero time, 1.0m*l* of a freshly prepared 2.0×10^{-3} M dioxane solution of BBIC was pipetted into 100m*l* flask containing 99.0m*l* of buffer solution.

The absorbance of BBIC derivatives was determined on Pye Unicam SP 500 Ultraviolet Spectrophotometer at λ_{max}.

The N-(Benzenesulfonyl)benzamide; the final hydrolysis products were identified by IR spectrum.

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Table 2. The change of absorbance (A) of N-(benzenesulfonyl)-benzimidoyl chloride at 273nm vs. time at pH 4.50 and 25°C

| [BBIC]=2.0×10^{-5} M			
Time(sec)×10^{-2}	A	Time(sec)×10^{-2}	A
3.78	0.360	10.71	0.270
5.93	0.328	13.26	0.247
8.79	0.300	14.86	0.230
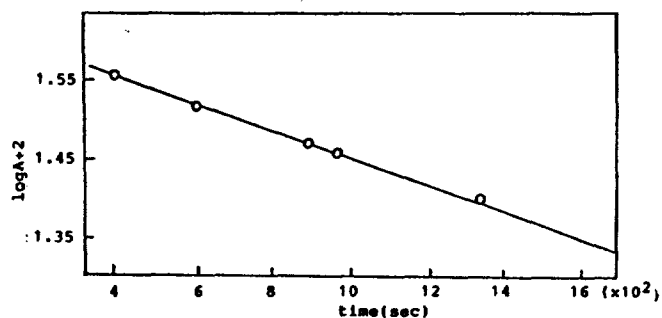
Figure 1. Logarithmic plots of absorbance (A) vs. time for the hydrolysis of N-(benzenesulfonyl) benzimidoyl chloride at pH 4.50, 25°C and 0.10 ionic strength.

Table 3. First-order rate constants for the hydrolysis of N-(benzenesulfonyl)benzimidoyl chloride at various pH and 25°C

Buffer solution	pH	k_{obs}(sec^{-1})	k_{cal}(sec^{-1})
HCl	0.50	3.44×10^{-4}	3.08×10^{-4}
	1.00	2.83×10^{-4}	3.08×10^{-4}
	1.50	2.21×10^{-4}	3.08×10^{-4}
	2.00	2.56×10^{-4}	3.08×10^{-4}
	2.50	2.62×10^{-4}	3.08×10^{-4}
	3.00	2.33×10^{-4}	3.08×10^{-4}
HAc+NaAc	3.50	2.80×10^{-4}	3.08×10^{-4}
	4.00	4.13×10^{-4}	3.08×10^{-4}
	4.50	3.83×10^{-4}	3.08×10^{-4}
	5.00	5.19×10^{-4}	3.08×10^{-4}
	5.50	2.92×10^{-4}	3.08×10^{-4}
	6.00	3.24×10^{-4}	3.08×10^{-4}
	6.50	2.80×10^{-4}	3.08×10^{-4}
$KH_2PO_4 + K_2HOP_4$	7.00	3.57×10^{-4}	3.08×10^{-4}
	7.50	2.98×10^{-4}	3.08×10^{-4}
$H_3BO_3 + NaOH$	8.00	3.40×10^{-4}	3.28×10^{-4}
	8.50	3.78×10^{-4}	3.55×10^{-4}
	9.00	5.53×10^{-4}	4.58×10^{-4}
	9.50	7.69×10^{-4}	7.82×10^{-4}
	10.0	1.78×10^{-3}	1.81×10^{-3}
	10.5	5.29×10^{-3}	5.05×10^{-3}
NaOH	11.0	1.53×10^{-2}	1.53×10^{-2}
	11.5	3.54×10^{-2}	4.77×10^{-2}

*The value is calculated according to the equation (2).

Results

The initial concentration of BBIC (2.0×10^{-5}M) was kept constant over wide pH range. Table 2 gives an example of
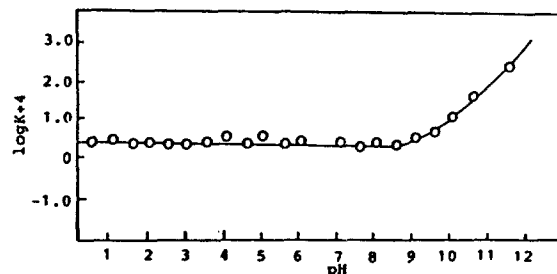
Figure 2. pH-rate profile for the hydrolysis of N-(benzenesulfonyl)-benzimidoyl chloride at 25 °C and 0.10 ionic strength.

Table 4. First-order rate constants for the hydrolysis of N-(benzenesulfonyl)benzimidoyl chloride derivatives at various pH, 25°C and 0.10 ionic strength

Buffer solution	pH	10 k_{obs} (sec^{-1})			
		p-CH_3	p-CH_3O	p-NO_2	m-NO_2
HCl	0.50	4.79	7.08	0.765	1.21
	1.00	5.65	7.24	0.582	1.13
	1.50	4.83	6.31	0.457	1.15
	2.00	5.28	5.89	0.462	1.00
	2.50	5.55	5.62	0.796	0.87
	3.00	5.03	6.76	0.627	7.97
HAc+NaAc	3.50	5.56	5.75	0.668	1.08
	4.00	6.34	5.75	0.668	1.11
	4.50	6.99	7.08	0.778	1.12
	5.00	6.37	5.62	0.562	1.27
	5.50	6.99	5.89	0.570	1.43
	6.00	6.97	7.41	0.753	1.79
	6.50	6.35	6.76	0.661	1.32
$KH_2PO_4 + K_2HPO_4$	7.00	6.50	4.89	0.661	1.23
	7.50	7.26	4.47	0.665	1.28
$H_3BO_3 + NaOH$	8.00	6.85	4.79	0.910	1.86
	8.50	6.47	5.01	1.41	4.39
	9.00	6.99	5.49	6.41	10.8
	9.50	7.08	6.61	30.5	57.5
	10.0	14.2	10.5	75.8	60.2
	10.5	26.5	17.8	152	187
NaOH	11.0	66.7	45.7		
	11.5	178	148		
	12.0	432	513		

the change of absorbance of BBIC with time at 273 nm and pH 4.50.

Figure 1 shows a logarithmic plots of absorbance (A) vs. time at constant pH. Under these condition, the observed rates of reaction were always the first order.

The first-order rate constants (k_t) obtained from these slops at various pH and 25 °C are given in Table 3 and Figure 2 shows pH-rate profile of this reaction. Table 4 are given rate constants of the other derivatives of BBIC determined by the same way.

Discussion

Determination of the Rate Equation for the Hydrolysis of BBIC: Analysis of Figure 2, log k_{obs} is plotted

Table 5. The change of rate constants for the hydrolysis of N-(benzenesulfonyl)benzimidoyl chloride with the concentration of sodium chloride at pH 4.50, 8.00 and 25 °C

NaCl (mole·l⁻¹)	$k_{obs}(sec^{-1})$	
	pH = 4.50	pH = 8.00
0.10	3.83×10^{-4}	3.78×10^{-4}
0.15	3.16×10^{-4}	3.57×10^{-4}
0.20	2.57×10^{-4}	3.90×10^{-4}
0.25	1.89×10^{-4}	4.42×10^{-4}
0.30	1.22×10^{-4}	3.68×10^{-4}
0.35	9.67×10^{-5}	3.77×10^{-4}
0.40	8.95×10^{-5}	3.90×10^{-4}

against pH; there are two different regions in this profile, each representing a different mechanism of hydrolysis;

$$Rate = - \frac{d[BBIC]}{dt} = k_{obs}[BBIC]$$

$$= \{k_o + k_{OH}[OH^-]\} [BBIC]$$

$$k_{obs} = k_o + k_{OH}[OH^-] \qquad (1)$$

were k_o is the pH independent part *i.e.,* it is the rate constant due to catalysis of H_2O and the second term is pH dependent part.

The k_o and k_{OH} for the hydrolysis of N-(benzenesulfonyl) bezimidoyl chloride can be calculated as followings: At pH 0.01—7.00, k_o takes 3.08×10^{-4} sec,⁻¹ which is the average value of observed rate constants. The value of k_{OH} is obtained from the slope of the straight line in Figure 2 *i.e.,* $k_{OH} = 15.0$ sec,⁻¹ is determined from the value $k_{obs} = 7.69 \times 10^{-4}$ sec,⁻¹ at pH 9.50 and $k_{obs} = 5.29 \times 10^{-3}$ sec,⁻¹ at pH 10.5.

Substituting these values into the equation (1) p-H, BBIC;

$$k_{obs} = 3.08 \times 10^{-4} + 15.0[OH^-]$$

$$= 3.08 \times 10^{-4} + 1.50 \times 10^{-13} / [H_3O^+] \qquad (2)$$

Figure 2 and Table 3 show that the values of over-all rate constant, k_{obs} calculated according to equation (2) are in good agreement with the observed values. Similarly, the rate equations obtained for the BBIC derivatives are as follows;

$$p\text{-}CH_3\text{-}BBIC : k_{obs} = 6.10 \times 10^{-4} \qquad (3)$$
$$+ 5.83 \times 10^{-14} / [H_3O^+]$$

$$p\text{-}CH_3O\text{-}BBIC : k_{obs} = 5.99 \times 10^{-4} + \qquad (4)$$
$$+ 3.91 \times 10^{-14} / [H_3O^+]$$

$$p\text{-}NO_2\text{-}BBIC : k_{obs} = 6.45 \times 10^{-5} \qquad (5)$$
$$+ 7.71 \times 10^{-13} / [H_3O^+]$$

$$m\text{-}NO_2\text{-}BBIC : k_{obs} = 1.19 \times 10^{-4} \qquad (6)$$

Salt Effect. The salt effects on the rate of hydrolysis of BBIC was observed with changing the concentration of chloride ion at pH 4.50 and 8.00 are summarized in Table 5.

As shown in Table 5, the value of rate constant was decreased as the concentration of chloride ion increased in low pH. However, in high pH, the rate is reasonably insensitive to the concentration of sodium chloride.

Table 6. Rate constants for the hydrolysis of N-(benzenesulfonyl)benzimidoyl chloride in mixed solvents at pH 4.50, 8.00 and 25 °C

Vol. (%) MeOH-H₂O	$k_{obs}(sec^{-1})$	
	pH = 4.50	pH = 8.00
90-10	1.76×10^{-4}	3.40×10^{-4}
80-20	2.01×10^{-4}	3.10×10^{-4}
70-30	2.97×10^{-4}	3.37×10^{-4}
60-40	3.83×10^{-4}	3.44×10^{-4}
50-50	4.65×10^{-4}	3.50×10^{-4}
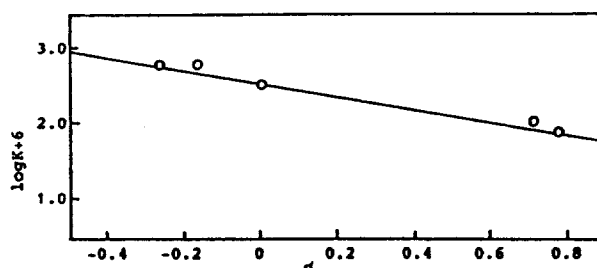
Figure 3. Hammett plot for the hydrolysis of N-(benzenesulfonyl)benzimidoyl chloride derivatives at pH 4.50 and 25 °C in 60% methanol.
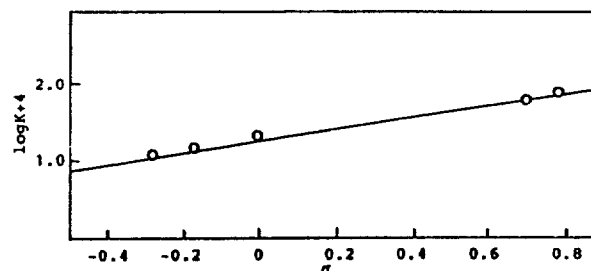
Figure 4. Hammett plot for the hydrolysis of N-(benzenesulfonyl)benzimidoyl chloride derivatives at pH 10.0 and 25 °C in 60% methanol.

Solvent Effect. To examine the effect of ionizing power of solvent on the rate of hydrolysis of BBIC was studied in various methanol-water mixture.

The results at pH 4.50 and 8.00 are given in Table 6. In low pH range, it is found that the rate of hydrolysis is facilitated with the increase of water content. These facts suggest that the hydrolysis proceeds through different mechanism at low pH and high pH.

Substituent Effect. As shown in Figure 3 and 4, at low pH, electron donating substituent accelerated ($\rho = -0.91$) the rate of hydrolysis, however, at high pH, retard the rate ($\rho = 0.94$). These results also suggested that the hydrolysis proceeds through different mechanism in acidic and basic media.

Mechanism of Hydrolysis of BBIC. The mechanism for the hydrolysis of BBIC at low pH is most reasonably formulated as S_N1 mechanism.

The kinetics, product, the effect of solvent, salt and substituent are in agreement with a following mechanism.

The formation of carbonium ion will be the rate-determining step. At second step, water molecule combines with carbonium ion to gives an unstable enol intermediate which rapidly converts to stable keto form. In low pH range, the
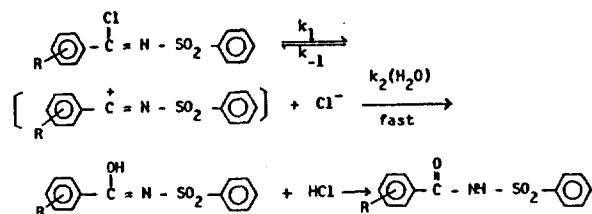
rate of hydrolysis facilitate with the increase of water content (Table 6).

This is as expected for $S_N 1$ mechanism. As shown by the Hammett plots of Fig. 3, at low pH, it is found that the rate is accelerated by a electron donating group with $\rho = -0.91$.

These results are interpreted in terms of stabilization of carbonium ion and acceleration of leaving of chloride ion by the electron donation group.

As shown in Table 5, the rate of reaction decreases as the concentration of chloride ion increases. This mass law effect is also explained by the following general rate equation for the reversible first step of $S_N 1$ reaction.

$$\text{Rate} = \frac{k_1 k_2 [BBIC][H_2O]}{k_{-1}[Cl^-] + k_2[H_2O]} = \frac{k_1 k_2 [BBIC]}{k_{-1}[Cl^-] + k_2} \qquad (7)$$

If the chloride ion concentration were constant, the rate becomes to $k_1[BBIC]$.

As shown in Figure 2 at high pH, the rate of hydrolysis of BBIC is proportional to the hydroxide ion concentration. The rate law and substituent effect could be interpreted in terms of a following $S_N 2$ mechanism:
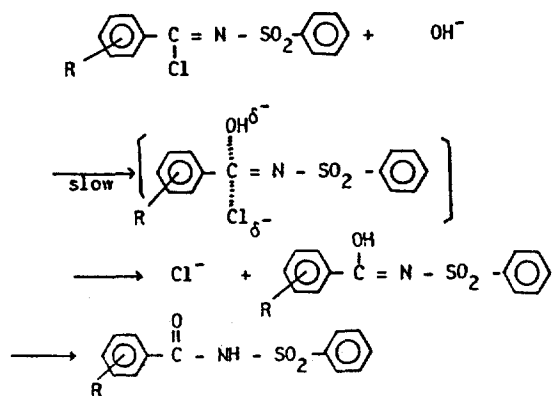
As would be expected from $S_N 2$ mechanism, the attacking of hydroxide ion to BBIC is accelerated by the electron withdrawing group as shwon in Figure 4 ($\rho = 0.94$). More-

over, from the positive value of ρ, it can be concluded that the bond formation is more important than the bond breaking at the transition state.

In the range of pH 7.00 − 9.00, it may be concluded that the $S_N 1$ and $S_N 2$ reaction occur competitively and the percentage of each reaction could be calculated by the rate equation, respectively.

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